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BIOLOGICAL BOARD

OF

CANADA

(formerly Contributions to Canadian Biology
and Fisheries)

Volume II, No. 1

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JANUARY-FEBRUARY

1936

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Printed by
THE UNIVERSITY OF TORONTO PRESS
for the
BIOLOGICAL BOARD OF CANADA

The Reduced Strychnine Method for Determining Nitrates in Sea Water

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(Received for publication May 4, 1934)

ABSTRACT

A satisfactory procedure for the estimation of the dissolved nitrates in the waters of the strait of Georgia is described involving the use of a Duboscq colorimeter. Seven ml. of sample and reagent plus 3 drops of concentrated hydrochloric acid develop a satisfactory colour. A large number of small glass vials are used in place of the regular Duboscq cups. Standards are prepared from random samples of sea water. The proportionality between colour developed and nitrate concentration is practically linear up to 4.8 mg. of NO_3 ion per litre but the factor is not 1. This necessitates an appreciable correction for all observed concentrations which differ greatly from that of the comparison standard.

Although considerable work has been done on the reduced strychnine method for determining dissolved nitrates in sea water (Harvey 1928a; Cooper 1932), certain serious difficulties were encountered in applying this method to the chemical analysis of water samples on board ship during an oceanographical program in the strait of Georgia. It became necessary to study the reaction more thoroughly with a view to making it applicable to the circumstances under which it would be used, with the result that the present investigation was carried out at the Pacific Biological Station, Nanaimo, B.C., during the summer of 1932.

I wish to thank the Biological Board of Canada for having made it possible to carry on this investigation, and to express my appreciation to Dr. W. A. Clemens and Dr. Neal M. Carter for their interest and advice.

PREPARATION OF REAGENT

After varying to a considerable degree the conditions during the preparation of the reduced strychnine reagent, it was concluded that in general practice the method given by Harvey (1928b) was the most satisfactory. One hundred and fifty grams of iron-free granulated zinc were washed with dilute hydrochloric acid, then with 100 ml. of a 0.25 per cent solution of mercuric chloride and finally with distilled water. The amalgamated zinc was placed in a well-washed flask with 25 ml. of water (distilled over baryta) and 2 g. of strychnine sulphate were added. An equivalent amount of strychnine appeared to be equally efficacious. One hundred and fifty to 200 ml. of concentrated hydrochloric acid were added, 50 ml. at a time, while the flask was warmed over an electric heater. There should not be any burner lighted in the room during the reduction as there is a certain amount of nitrate formed in the flame. The degree of heating

and rate of addition of the acid were so adjusted that a slow, continuous evolution of hydrogen from the zinc ensued over a period of 12 to 24 hours. The heating may be interrupted if necessary (Cooper 1932) and the mouth of the flask should be kept covered with an inverted beaker during the entire preparation. When the reduction was complete the solution was evaporated to a volume of 100 to 125 ml., or until the first suggestion of an olive-green colour appeared, then allowed to cool. One litre of nitrate-free sulphuric acid was then added very slowly to prevent loss by foaming. After the mixture had stood for several hours in order to allow the deposition of the zinc sulphate, the supernatant liquid was decanted and stored in brown glass bottles.

It was found that one-third the recommended quantity of zinc could be employed for the reduction if the rate of solution was decreased by adding the hydrochloric acid in smaller portions and at less frequent intervals. The development of an appreciable red coloration in the reagent due to traces of iron in the zinc is thus minimized.

In an attempt to reduce still further the time required for the reduction, other metals such as aluminium and magnesium were used which have a higher reduction potential. In each case, however, the reagent was not so sensitive to nitrates.

Nitrate-free sulphuric acid was obtained by heating the ordinary C.P. acid to 300° C. with a few crystals of ammonium sulphate (Cooper 1932). Atkins (1932) has suggested a method using hydrogen sulphide, which was not investigated in the present study.

Standards were prepared from chemically pure potassium nitrate powdered in an agate mortar and dried over calcium chloride at 110° C. for four hours. One stock solution was made up to contain 10 mg. of NO_3 ion per litre with water which had been distilled over baryta and which gave a negative test for dissolved nitrates. A second stock solution was made up to the same concentration with sea water which gave a negative test for nitrates ("nitrate-free" sea water). These solutions were preserved with one drop of toluene and were diluted to provide less concentrated standards as needed.

PRELIMINARY EXPERIMENTS

Preliminary tests were made by treating 5 ml. of several standards in 100 ml. Nessler tubes with 3 drops of concentrated hydrochloric acid and 5 ml. of reagent. The mixtures were shaken and allowed to stand for one hour, then diluted to 100 ml. A few such tests demonstrated that direct matching of the colour intensity in the open tubes permitted too great an error for satisfactory analysis. A specially constructed colorimeter (Carter and Tully MS.) containing a Duboscq colorimeter eyepiece mounted over two incased, tall Nessler tubes was much more satisfactory for this matching, but consideration of all the factors involved indicated that the alteration of the colour produced in the concentrated acid solution upon dilution to 100 ml. was introducing other errors. Hence it seemed advisable to make a study of the reaction, using a Duboscq colorimeter for the comparison of the colour intensities developed in the concentrated acid solutions.

The main error observed in working with the undiluted samples was now found to be due to the wide range of colour intensities developed when colour standards were made up from the same solution. This error is strikingly shown in table I which presents the results obtained when three 5-ml. samples, prepared from "nitrate-free" sea water to contain 0.20 mg. of NO_3 per litre, were treated with 5 ml. of reagent and 3 drops of concentrated hydrochloric acid. The tubes were matched in the Duboscq colorimeter against four standards made from "nitrate-free" sea water to contain 0.30 mg. of NO_3 ion per litre. All seven tubes were prepared simultaneously and subjected to the same conditions.

TABLE I. Errors encountered in preliminary colour comparisons of known concentrations of nitrate ion against standards

Sample	Actual concentration	Concentration calculated after comparison with four standards of concentration 0.30			
		(1)	(2)	(3)	(4)
1	0.20	0.18	0.08	0.20	0.08
2	0.20	0.26	0.11	0.25	0.08
3	0.20	0.19	0.10	0.12	0.05

Concentration unit: milligrams of NO_3 ion per litre.

The apparent concentrations of the three samples as calculated after comparison with the standards showed errors ranging from 30 per cent too high to 75 per cent too low. Such results could not be relied upon to give a quantitative representation of the changes in concentration of dissolved nitrates in oceanographic work. It was therefore important to investigate the reaction somewhat more thoroughly in order to fix the conditions necessary to secure consistent and concordant results.

PROPORTION AND CONCENTRATION OF REAGENT

The optimum concentration of reagent for a given quantity of sample was determined by treating ten 5-ml. portions of a standard solution of nitrate with as many different concentrations of reagent, prepared by diluting the stock reagent with "nitrate-free", concentrated sulphuric acid. The concentrations of these diluted reagents varied from 10 per cent to 100 per cent of that of the stock reagent and the volume added to the sample was in each case 10 ml., in order to secure a uniform evolution of heat upon mixing with the sample. After the mixtures had stood in the dark for one hour, the relative intensities of colour developed were determined in the Duboscq colorimeter. The results obtained with standards of concentration 0.5 and 4.0 mg. of NO_3 ion per litre (representative low and high nitrate concentrations encountered in local waters) are shown in table II. Although there was some difference between the experimental technique used in this series and that of the method described later and finally adopted, the results show that the optimum ratio of volume of stock reagent to volume of sample is in the neighbourhood of 1:1. It was concluded that the

TABLE II. Determination of the effect of reagent concentration on colour intensity developed

Conc. of sample* (volume = 5 ml.)	Volume of reagents added		Reading on Duboscq colorimeter	Relative calculated concentration from value (*) chosen as standard
	Stock reagent ml.	Conc. H ₂ SO ₄ , ml.		
0.5	1	9	23.1	0.073
	2	8	10.0	0.165
	3	7	8.0	0.206
	4	6	4.8	0.345
	5	5	3.3	0.500*
	6	4	3.4	0.475
	7	3	3.5	0.471
	8	2	3.6	0.457
	9	1	3.8	0.436
	10	0	4.0	0.412
4.0	1	9	22.2	0.568
	2	8	10.0	1.28
	3	7	7.9	1.62
	4	6	4.5	2.74
	5	5	3.2	4.00*
	6	4	3.2	4.00
	7	3	3.4	3.77
	8	2	3.5	3.66
	9	1	3.6	3.54
	10	0	3.8	3.36

*Concentration unit: milligrams of NO₃ ion per litre.

reagent made up according to Harvey's method (1928b) is apparently that best suited for general use.

TYPES OF STANDARDS

A comparison of six nitrate standards made up in distilled water with six others made up to the same concentrations in "nitrate-free" sea water indicated that there is an inhibiting factor which causes less colour to be developed in the sea water standards (figure 1). It would therefore appear advisable in practice to use standards which closely approximate the composition of the water being analyzed; that is, when estimating the nitrates in sea water the standards should be made up in "nitrate-free" sea water.

EFFECT OF TIME AND TEMPERATURE

The next factors investigated were the effect of time and temperature on the development of colour. One series of four tubes containing 5 ml. of sea water with a nitrate concentration 0.3 mg. of NO₃ ion per litre and another series containing 2.5 mg. of NO₃ ion per litre were prepared. To each tube were added 3 drops of concentrated hydrochloric acid and 5 ml. of reagent. At the end of 1, 18, 50 and 90 hours standing in the dark at room temperature, the

colour intensities were matched against one tube of appropriate concentration, chosen as a standard. The results are shown in table III and indicate that under these conditions of preparation and standing, the reaction is very slow in reaching equilibrium. When the reactants were kept at 74° C. equilibrium was

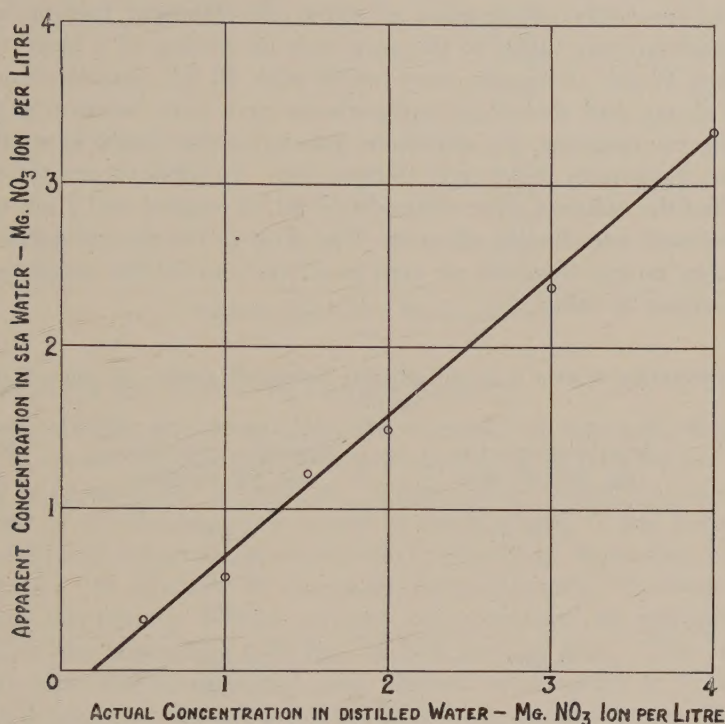


FIGURE 1. Colour developed (expressed as apparent concentration) in nitrate standards made up to various concentrations in "nitrate-free" sea water, as determined by matching against standards made up to the same concentrations in distilled water.

TABLE III. Effect of time on development of colour intensity

Sample	Actual concentration	Calculated concentration after			
		1 hr.	18 hr.	50 hr.	90 hr.
1	0.30	0.30*	0.30*	0.30*	0.30*
2		0.26	0.34	0.30	0.28
3		0.31	0.33	0.32	0.28
4		0.35	0.33	0.33	0.28
5	2.50		2.50*	2.50*	2.50*
6			1.94	2.42	2.48
7			2.20	2.50	2.50
8			2.00	2.42	2.47

*Chosen as standard for comparison. Concentration unit: milligrams of NO₃ ion per litre.

attained much more rapidly and colour comparisons after one hour at this temperature gave results quite as uniform as those obtained after other samples had remained several hours at room temperature.

Since the determination of nitrates was to be done on board ship and application of heat was difficult or entirely impracticable, other methods of obtaining the necessary acceleration of colour development had to be investigated. Advantage was taken of the slow rate of cooling of a large volume of liquid. When 10 ml. of reagent were mixed with 10 ml. samples, cooling took place quite slowly and the colour comparisons gave very uniform results. In order to conserve reagents, the minimum quantities that could be used without reducing the uniformity were next determined. Consistent results were still obtained when the volumes were reduced to 7 ml. of reagent and 7 ml. of sample, and these volumes were finally adopted. The error in the determinations carried out in this way ranged from 0.0 per cent to 5.2 per cent of the amounts actually present, as shown in table IV.

TABLE IV. Percentage of error in colour intensity developed, using 7 ml. each of reagent and sample

Sample	Actual concentration, mg. NO ₃ ion/litre	Calculated concentration, mg. NO ₃ ion/litre	Per cent error
1	0.20	0.200*	...
2		0.201	0.5
3		0.197	1.5
4		0.206	3.0
5	0.50	0.500*	...
6		0.508	1.6
7		0.474	5.2
8		0.500	0.0
9		0.475	5.0
10		0.496	0.8
11		0.498	0.4
12	4.00	4.00*	...
13		3.82	4.5
14		3.92	2.0
15		4.20	5.0
16		4.06	1.5

*Chosen as standard for comparison.

Similar uniformity of results was obtained using as little as 5 ml. of sample and 5 ml. of reagent, by placing the tubes for one hour in a nest of cotton wool or asbestos, whereby the rate of cooling was considerably decreased. If the tubes were still above room temperature at the end of the hour they were allowed to cool before comparison in the Duboscq colorimeter. The results are shown in table V.

TABLE V. Percentage of error in colour intensity developed, using 5 ml. each of reagent and sample (insulated)

Sample	Actual concentration, mg. NO ₃ ion/litre	Calculated concentration, mg. NO ₃ ion/litre	Per cent error
1	0.50	0.50*	...
2		0.48	4.0
3		0.502	0.4
4		0.51	2.0
5		0.49	2.0
6	4.0	4.0*	...
7		3.82	6.0
8		3.92	2.0
9		4.20	5.0
10		4.06	1.5

*Chosen as standard for comparison.

PROPORTIONALITY OF COLOUR TO CONCENTRATION

Harvey (1928b) has shown that the intensity of colour developed is proportional to the nitrate concentration up to 0.575 mg. of NO₃ ion per litre. This range had to be extended in order to include nitrate concentrations frequently encountered in the waters of the strait of Georgia, and it was found that the proportionality of colour to concentration is somewhat dependent on time and other factors. In figure 2 is shown the proportionality of colour developed in solutions containing various nitrate concentrations as compared to that developed in one containing 0.26 mg. of NO₃ ion per litre. The comparisons were made after the samples had been allowed to stand for 1, 2, 6, 8 and 24 hours. It is seen that there is a linear relation extending over the lower portion of the concentration range and that up to the end of 6 hours the slope of this line differs from 1, the theoretical value. As the time increases there is a progressive shift of the slope which is due to two factors: (a) there is proportionally more colour developed in a short time in the solutions of high nitrate concentrations than in those containing little nitrate, while those containing the smaller quantity develop their maximum colour more quickly; (b) the solutions of high concentration begin to fade after a few hours, leaving the dilute solutions with almost their original colour even after 8 hours. This fading effect is graphically shown in figure 3 where the colour intensity developed after 2 hours was taken as a standard against which the intensities developed after 6 and 24 hours were compared.

It can be seen from figure 2 that with increasing time the colour intensities developed in the lower concentrations gradually approached the theoretical values and if it were not for the more rapid fading in the higher concentrations, it is probable that a uniform proportionality of colour to concentration would result. However, since it is not practicable to leave the solutions for any great length of time, an advantageous period of colour development appears to be one hour. At the end of this time the relation of apparent to true concentration

is almost linear between the concentrations of 0.2 and 4.8 mg. of NO_3 ion per litre, which include all of the concentrations found in local waters. A correction can then be applied to the results obtained in order to counteract the departure of the linear relation from its theoretical slope of 1. This may be done most readily from a correction graph similar to figure 2, constructed from the values obtained in a series of experiments with the reagent used and the types of sea water encountered.

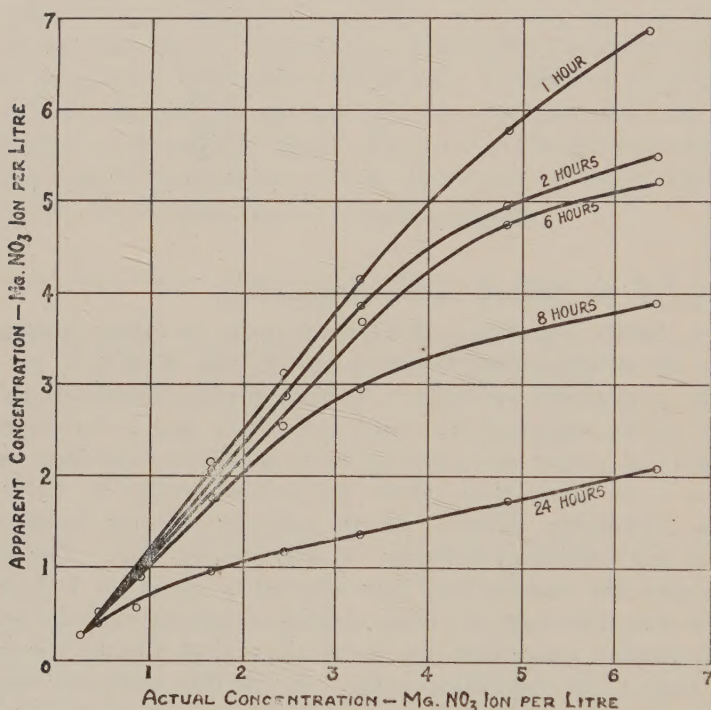


FIGURE 2. Relation of colour developed (expressed as apparent concentration) to actual concentration of nitrate ion, as determined by matching against standard of lowest concentration after various time intervals.

DILUTION PREVIOUS TO COLOUR COMPARISON

The possibility of diluting the solutions (after colour development) for comparison in tall Nessler tubes was again investigated in the light of the foregoing experimental results. Seven millilitres each of sample and reagent, plus 3 drops of concentrated hydrochloric acid, were mixed in a Nessler tube with precautions against splashing either the sample or reagents on the walls of the tube. Thorough mixing was necessary but excessive shaking hastened the cooling and impaired the uniformity of the results. After allowing the requisite time for colour development, distilled water was added until the total volume was 100 ml. The solution was thoroughly mixed by inverting the tube six times and the colour then compared with a chosen standard in the modified colorimeter previously

mentioned. Dilution was effected with (a) distilled water, (b) "nitrate-free" sea water, and (c) sea water containing 8 mg. of NO_3 ion per litre. The object of investigating sea waters as diluents was to effect a possible conservation of distilled water on board ship. The results given in table VI show that there was little difference between the values obtained after diluting with sea water containing a comparatively high nitrate concentration, and those obtained after

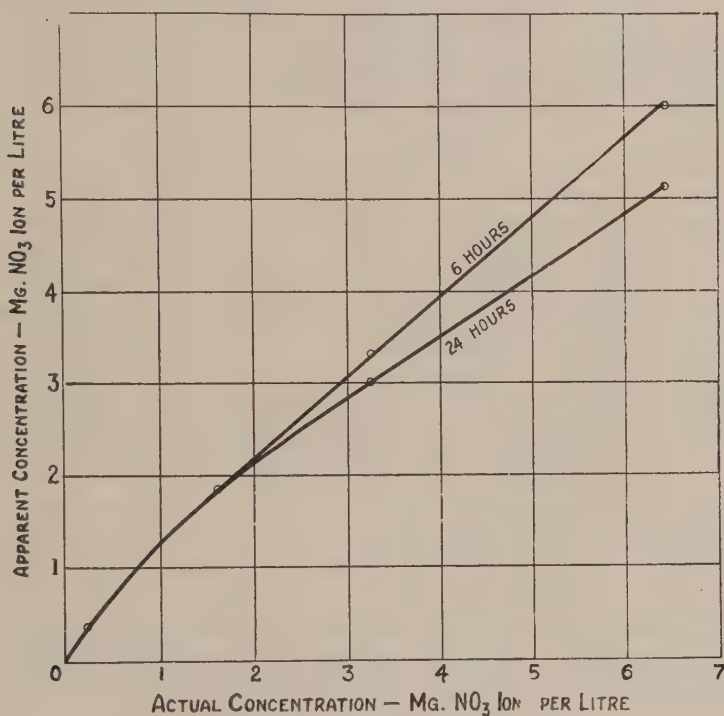


FIGURE 3. Fading of colour (expressed as apparent concentration) in solutions which had stood for 6 and 24 hours before being matched against solutions of the same concentrations which had stood for 2 hours.

TABLE VI. Effect of dilution of colour with different types of water for comparison of colour in tall Nessler tubes

True conc.	Calculated concentration after dilution with		
	Distilled water	NO_3 -free sea water	Sea water containing 8 mg. NO_3 per litre
0.5	0.500*	0.545	0.572
0.5		0.572	0.584
4.0	4.00*	4.26	4.03
4.0	3.96	4.18	4.32
8.0	8.00*	8.60	8.75
8.0	8.40	8.90	8.41

*Chosen as standard for comparison.

dilution with "nitrate-free" sea water. This is explicable on the supposition that, lacking heat of reaction and sufficient time, the reagent is insensitive to further additions of nitrates. The values in both of the above series were considerably higher than the theoretical values and also higher than when distilled water was used as a diluent.

It was found that the standards for comparison had to be made up, before addition of the reagents, to approximately the same concentration as the samples, since dilution of the standards to definite concentrations after the development of the colour produced a yellow tint which could not be satisfactorily matched against the pink or red colour of the sample.

CONCLUSION

Owing to the uncertainty of the colour tint developed in standards prepared as described in the last section, the most satisfactory method of nitrate determination was found to be that of direct comparison of the undiluted samples in the Duboscq colorimeter. Seven ml. of sample and reagent, plus 3 drops of concentrated hydrochloric acid, are used for the development of the colour. A large number of small glass vials are used in place of the two cups supplied with the instrument. In view of the difficulties encountered in obtaining "nitrate-free" sea water for the preparation of standards, these may be prepared from random samples of sea water by means of a technique described by Carter and Tully (MS.).

SUMMARY

1. The method given by Harvey for the preparation of the reduced strychnine reagent gives very satisfactory results and the reagent so prepared is of the optimum concentration. Metals other than zinc were found less satisfactory for the reduction.

2. High concentrations of nitrate develop in a short time proportionally more colour than low concentrations, but they attain their maximum colour intensity more slowly.

3. Fading of the colour developed begins to be appreciable after 6 hours. Low concentrations do not fade appreciably in 8 hours.

4. The relation between colour developed and concentration of nitrate is practically linear up to 4.8 mg. of NO_3 ion per litre, but the slope of the curve differs from the theoretical value of 1. This necessitates an appreciable correction for all observed concentrations which differ greatly from the comparison standard.

5. In order to secure consistent results, at least 7 ml. of reagent and 7 ml. of sample, plus 3 drops of concentrated hydrochloric acid, should be employed. The proportion of sample to reagent should always be 1:1 and all solutions should be allowed to stand an equal time (at least one hour and not more than two).

6. Comparisons should be made against standards of approximately the same salinity, containing approximately the same nitrate concentration.

7. Colour comparisons are best performed with the undiluted mixtures in a colorimeter of the Duboscq type, as dilution for comparison in Nessler tubes is likely to introduce anomalies in colour tint.

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Fish Oils. VI. The Structure and Properties of Pilchard Oil Films

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(Received for publication December 12, 1935)

ABSTRACT

British Columbia pilchard oil dries more rapidly than linseed oil and yields substantial protective films. The films are softer and more tacky than those from linseed oil. They are more permeable to moisture, and show a tendency to become dull and to bloom. These defects can partly be corrected by the use of the proper drier combinations and incorporation of gums but they can be entirely eliminated only by steam distillation of the polymerized oil at high temperatures. The product of this treatment yields films superior to those of other drying oils in hardness, gloss, lower permeability and freedom from yellowing and blooming.

The structure and properties of the films are discussed. The nature and distribution of the non-drying components in the film are described. Methods for estimating permeability and moisture absorption of films given and the influence of moisture as the primary agency in film disintegration is emphasized. The nature of yellowing, cissing and blooming, and methods for correcting these defects in pilchard oil are also discussed.

This paper is the third of a series concerning the drying properties of British Columbia pilchard oil. The first two publications dealt with the influence of various treatments and catalysts on the bodying and oxidation of the oil. It is the purpose of the present paper to treat with the properties of the solid films.

The main object of the study of film properties was to find methods of correcting certain defects which are common to films of all drying oils but are especially pronounced in drying fish oils. These defects and methods for correcting them are described in the present paper.

THE IDEAL PROTECTIVE FILM

A good film should possess the following properties. It should dry rapidly to give a smooth even surface and should be adhesive, tough, distensible and elastic so as not to crack with expansion of the under surface. Chemically, it should be inert to oxygen, acids and alkalies. Furthermore, it should remain stable to light and moderately high temperatures. From a decorative standpoint it should be transparent and colourless so as not to mask the colour of pigments or dyes that may be incorporated. Whether or not it should be impermeable to moisture depends somewhat on the nature of the material to be coated. For porous materials like wood, which often contains a considerable amount of moisture, a certain degree of permeability in a coating enables moisture to escape,

thereby preventing blistering and peeling. For metals and other non-porous materials on the other hand, waterproof films are desirable.

Few commercial protective coatings—drying-oil films in particular—approach this standard. For example, linseed oil, the most important of drying oils, yields films that tend to dry hard and brittle. Consequently they crack when stretched. They are unstable to oxygen and alkalis, and turn yellow in the absence of white light. Also, they are quite permeable to moisture and on prolonged exposure, swell and lose their transparency. Fish oil films (from raw oils) possess even less merit. They are less stable chemically, more permeable to moisture and exhibit a more pronounced yellowing tendency. Furthermore, they are soft and tacky, tending to collect dust and become dull. On the other hand they are more flexible and extensible than linseed oil films.

THE DRYING OF FILMS

The transition from liquid to a solid film involves many complex chemical and physical changes which as yet are vaguely understood. Numerous suggestions as to the mechanism of the process have been submitted by Blom (1927), Wolff (1928), Eibner and Rossman (1928), Auer (1929), Morrell and Marks (1929), Wilborn (1929), Long (1930) and other investigators, but the various theories only go to emphasize the extreme complexity of the drying process. Chemically, many types of reaction are involved, including oxidation, condensation, polymerization, and isomerization. Furthermore, the character, rate and order of the chemical events are influenced by factors such as temperature, humidity, light, catalysts and initial processing of the oil. The accompanying physical changes are equally obscure. It is fairly well established, however, that drying involves four main stages, namely: (1) a period of induction, (2) formation of micelles, (3) coagulation of micelles to form a gel, and (4) subsequent changes in the gel. As these changes progress the oil decreases in unsaturation and increases in viscosity. With the onset of coagulation the film begins to take on a definite structure, the nature of which may vary, depending upon the sequence of chemical changes and hence on conditions of drying. Though possessing a definite structure, the film during gel formation is still fluid and sticky. It is not until the fourth stage that actual drying or solidification occurs. The final structure is usually modified further by the presence of components which are non-drying and therefore do not contribute towards film formation.

Under normal conditions of drying, oxygen of the air is the chief initiator and promoter of the drying process. It appears, however, that the first three stages of the process may be accomplished without oxygen, as for instance by steam polymerization. It has been stated in a previous paper in this series (Brocklesby and Denstedt 1934) that pilchard and other oils may be converted into elastic, rubbery gels by blowing the oils with superheated steam. The product is a pale-coloured, tenacious gel which appears to be a rubbery solid but actually is an extremely viscous fluid. Figure 1 shows the close similarity between such a gel produced by steam polymerization at 300°C. (a), and one obtained by blowing pilchard oil with air at 200°C. (b). The former, produced in

the absence of oxygen, is pale in colour, transparent and odourless, while the air-blown product is dark-coloured and smells strongly of the breakdown products of oxidation.



FIGURE 1. **a**,—Pale-coloured, transparent rubbery product produced by steam-blowing pilchard oil at 300°C. **b**,—Dark opaque rubbery product from blowing pilchard oil with air at 200°C. **c**,—The under and upper sides of an oven-dried pilchard oil film (dried over mercury), which had been immersed in distilled water for a week. The under surface “blooms” and becomes dull and opaque while the upper layer of the film retains its normal gloss and transparency. **d**,—Cross-section of a wrinkle of a moisture-saturated linseed oil film, as viewed through crossed nicols. The inner portion of the film is opaque whereas the surface layer is clear and transparent (the light area at the upper left is the film surface and is to be disregarded). **e**,—Cross-section of a moisture-saturated pilchard oil film viewed through uncrossed nicols. Note the clear outer layers and the opaque inner layer with cavities. This film was dried on both sides hence two clear layers.

It is argued by some investigators that since it is practically impossible to obtain an oil absolutely free from oxidative products and since these are strongly catalytic to the drying process, it is impossible to produce a gel even by steam- or vacuum-bodding without the aid of oxygen or a trace of oxidative product. Whether or not this be so, it is certain that the fourth stage of drying, namely

the conversion of the tenacious semi-solid gel into a dry, tough, rubbery solid product cannot be brought about without an ample supply of oxygen. Thus, the gel from steam-bodying remains sticky and fluid until exposed to air, when it is converted into a tough product entirely free from tackiness, and which is also stronger, more dense but less extensile. Evidently oxygen is essential for this change and since it has been shown in a previous paper that oils polymerized in the presence of oxygen yield products of higher molecular weight than those polymerized in its absence, it is apparent that intermolecular oxygen linkages play an important part. Under normal conditions of drying the formation of these linkages begins early in the drying process, increasing to a maximum during the last stage. In the case of the bodying of oil by heating in the presence of air or by blowing, although oxidation is extensive, the formation of oxygen linkages does not appear to occur to any great degree, probably because of the low solubility of oxygen in the oil at higher temperatures and the low stability of these intermolecular linkages under such conditions. This would account for the differences in structure of gels produced during normal drying and those from artificial bodying, as evidenced, for example, by the relatively extensive contraction that bodied oils undergo during solidification.

Long and co-workers (1929) have shown that the volume and area of fatty acid molecules increase on oxidation. Also since oxidation produces changes in polarity, it is to be expected that during drying the molecules of the film undergo a series of orientations. This is suggested by the behaviour of oil when spread on a mercury surface. Thus, when a small amount of oil (containing drier) is dropped on a large clean mercury surface, it spreads instantly over a large area in a very thin film usually showing diffraction colours at the periphery. As oxygen is taken up, the peripheral portion undergoes many alternate expansions and contractions, finally breaking up into a number of fantastically shaped tendrils which gradually become narrower until they break up into islets or globules. Doubtless these changes are also closely associated with the phenomenon of wrinkle formation characteristic of thick films, especially when they contain very active driers. Wrinkle formation can easily be observed if mercury in a petri dish is completely covered with a fairly thin oil film. On exposure, the film soon becomes finely rippled, the troughs of the ripples being so thin as to make the mercury appear exposed. In time the rippled pattern becomes coarse, finally giving rise to wrinkles and folds. It is interesting to note that the ripples are formed long before any solid surface film is detectable. These phenomena, therefore, appear to involve some sort of molecular orientation at the surface due to changes in molecular volume and possibly also the surface tension at the air-oil interface. Wrinkling is most extensive with rapid driers such as cobalt and manganese. Slower driers like lead, cerium and copper give rise to much less marked disconformities, the type of wrinkling usually taking the form of an alligatored pattern.

THE DRY FILM

Since oxidation occurs more rapidly at the exposed surface it is obvious that solidification begins there and proceeds inwards. The film, therefore, consists

of two more or less distinct layers, namely: the solid surface layer and the inner less compact portion. In a solid film these layers can be shown in various ways. The simplest method is to cut through a piece of the film with a knife-edge by very gradually increasing the pressure. In this way the comparative toughness of the two portions is easily discernible. If the film has been oven-dried, the surface portion will be hard and brittle and can easily be separated from the

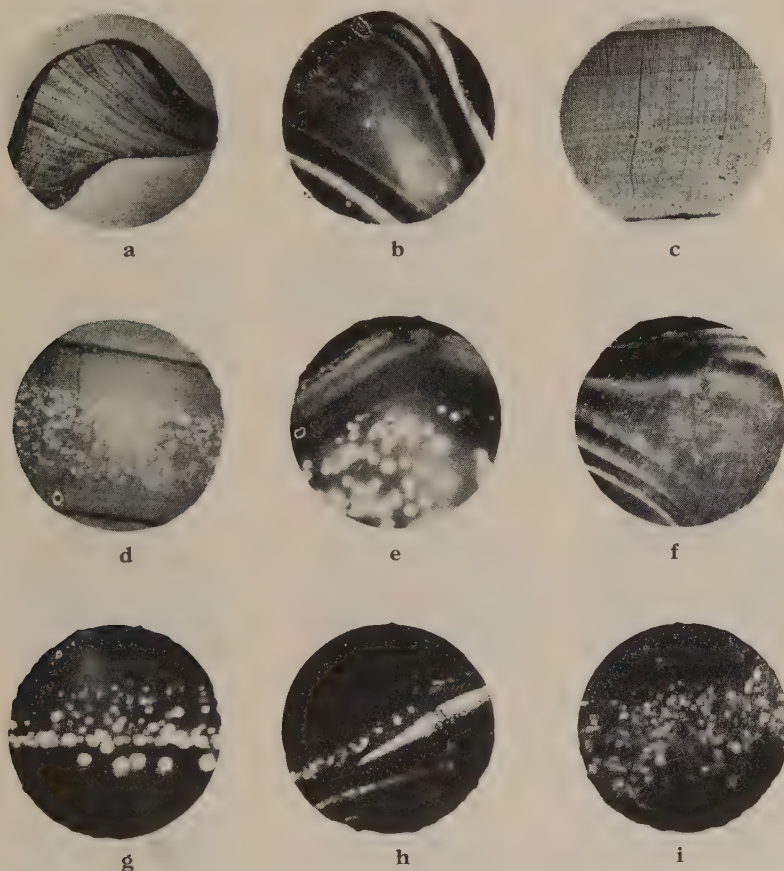


FIGURE 2. **a**,—Section of wrinkle of linseed oil film viewed through uncrossed nicols. Dark outer areas are surfaces of the film to be disregarded. **b**,—Section of linseed oil film wrinkle viewed through crossed nicols. Note the clear surface layers and the less dense inner portion containing crystalline solids. **c**,—Section of pilchard oil film under uncrossed nicols. Film diam. 1.4 mm. **d**,—Section of pilchard oil film under half-crossed nicols. Note the inner portion of film which is less dense and contains crystalline bodies. **e**,—Section of pilchard oil film showing transparent clear outer layer and softer inner portion containing solid crystalline masses. Viewed under half-crossed nicols. **f**,—Section of a linseed oil film showing the relative absence of crystalline solid components in the inner portion. Half-crossed nicols. **g**,—Crystalline portion of pilchard oil film as viewed through fully crossed nicols. **h**,—Section of a wrinkle of a menhaden oil film—under crossed nicols. **i**,—Inner portion of a pilchard oil film showing spherocrystalline character of many of the solid masses. Crossed nicols.

softer underlayer. Or if such a film be placed between felt pads moistened with a solvent such as chloroform, the two layers separate spontaneously, due to differential swelling. Still another method is to soak the film in water. After a few days the inner, semi-solid portion will have become dull and translucent while the surface solid part retains its transparency. This is illustrated in figure 1, c-e.

With continued exposure, solidification gradually proceeds inward. Catalysts and high temperatures tend to accelerate the process but at the same time produce a more compact surface structure which retards the entrance and diffusion of oxygen.

From the foregoing discussion one might infer that the film when ultimately solidified throughout will show a homogeneous structure. That this is not so, is illustrated in figure 2, a and b, of film cross-sections as viewed through the polarizing microscope.

It is apparent that the film still consists of two layers, the outer being homogeneous and the inner, although transparent, being quite conglomerate in its makeup. This type of structure is much more pronounced in fish oil than in linseed films and is due to the accumulation of solid non-drying compounds in the under layer. How these solids accumulate is not definitely known, but it is probable that as the surface layer solidifies and becomes more compact the non-drying and semi-drying components become insoluble in that layer and are thus forced into the interior of the film . . . a phenomenon similar to the crystallization of solid glycerides from polymerized oils (see Brocklesby and Denstedt 1934). This process is evidenced also by other experiments. Thus, if a film which has been dried for several days in the oven (on mercury), is reversed and left in the oven until the liquid underside has thoroughly dried, a cross-section will reveal the solid constituents sandwiched between two clear surface layers (see figure 2, c and d). It is apparent from these observations that the inner portion of a film differs from the outer layer not only in degree of oxidation and completeness of structure, but also in its composition.

Long and co-workers (1928) in their study of adsorption of liquids by drying oil gels, have shown after Langmuir that the liquid components of linseed oil films are not held in the films by mechanical entrainment within the film meshes, but are adsorbed on the walls of the capillaries. With aging of the film the drying members of these adsorbed components are gradually built into the film structure. The inner portion of the film therefore becomes denser and tougher with age. The same is true of the liquid components of pilchard oil films and probably of the solid components in freshly dried films. On aging of the films, however, as indicated in the photographs, the solids collect into crystalline masses and then are held mechanically in the film structure.

SOLID CONSTITUENTS OF FILMS

It is convenient at this point to describe a few interesting characteristics of the solid materials in pilchard oil films. In freshly prepared films these solids are distributed in finely divided form, uniformly throughout the film except in the clear layer at the surface. This layer is perfectly transparent and free from solids. On aging of the film, the small particles in the inner portion gradually collect to form larger spherical crystalline masses consisting of small needle-like crystals radiating from a centre. Under polarized light they appear as shown in figures 2, e-h.

In oven-dried films the crystalline region is almost confined to the innermost part of the film indicating that the solids are squeezed out of the highly oxidized surface layer of the film.

The films shown in the figures were dried over mercury in an oven at 60°C. They were made from raw and bodied oils with and without driers. Cobalt driers gave rise to large coarse wrinkles, sections of which are shown in some of the photographs.

On continued aging, the solid aggregations increase in size, thus indicating a tendency towards the reduction in surface area of the film capillaries accompanied by a squeezing-out action. Furthermore, many of the solid masses take on a peculiar crystalline form illustrated in figures 2i and 3a-e, thus indicating a more compact crystal structure. In convergent white light under crossed nicols the crystals show typical uniaxial interference figures with alternating dark and coloured concentric rings as illustrated. The spherical crystalline masses vary in diameter and are commonly seen in aged sections of oven-dried pilchard oil films but have not been detected (by the writers) in linseed oil films although very similar, but smaller, spherical bodies have occasionally been detected in liquid commercial cobalt linoleate drier.

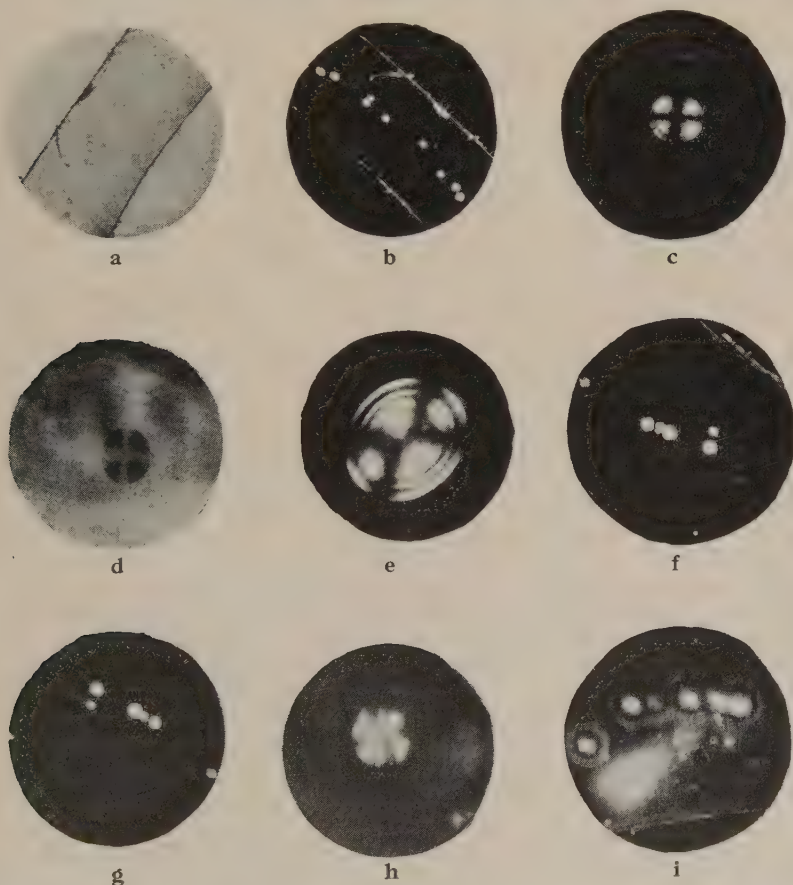


FIGURE 3. **a**,—Pilchard oil film, uncrossed nicols. **b**,—Same film as in **a** under crossed nicols. **c**,—Higher magnification of an individual sphero crystal under crossed nicols. **d**,—Same as **c** under slightly crossed nicols. **e**,—Crystal still more highly magnified. **f**,—Sphero crystals before melting. **g**,—Crystals solidified after melting. **h**,—Partial reversion of a melted and resolidified crystal to the sphero state. **i**,—Diffusion of solid crystalline material through the film a few days after having been melted.

The crystals melt readily when the section is heated and solidify again on cooling. Under crossed nicols the field remains dark until the cooling masses solidify, when they appear suddenly as bright spots in the surrounding dark area. On melting and resolidifying, they become somewhat distorted from their former true spherical form (figure 3g) and no longer show interference bands. Some crystals in the course of a few days again show signs of structural change—as illustrated in figure 3h. Others, particularly if kept in the melted condition at temperatures considerably above their melting point for a few minutes, behave in a different manner. If these are examined from day to day, it will be observed that some of the solid masses appear to disperse again throughout the film (figure 3i). This movement of solid glycerides and fatty acids through the film network occurs extensively in films from polymerized pilchard oil and in oven-dried films, and accounts for one of the phenomena known as "blooming", discussed later (cf. page 39). The movement is facilitated by fluctuations in temperature and humidity.

The solid substances along with some liquid may be extracted from films by means of hot absolute alcohol. On concentrating and cooling the solution, the solids precipitate in a pure white crystalline form. Analysis has shown the material to be a mixture of saturated glycerides and fatty acids. On heating carefully the crystals soften at about 49°C. and the bulk of them melt between 55 and 57°C. The mixture contains also a small proportion of solid which melts at about 80°C. On cooling, the mixed product solidifies to a typical hard, white, waxy fat.

INFLUENCE OF CATALYSTS

The same catalysts used in the work on the oxidation of pilchard oil have been employed in the present experiments on the film properties. Although various oxides and salts were examined most of the work was done with the metallic soaps because of their superior solubility. The influence of some of these metallic soaps on the gain in weight and drying time of pilchard oil is recorded in table I.

As in the case of other oils, cobalt and manganese surpass all other metals in their drying activity with pilchard oil. Cobalt is superior in many respects to manganese. Apart from its superiority as an accelerator, it imparts less colour and produces harder and less tacky films. In addition it has a lesser tendency to precipitate out as the soaps of the solid fatty acids, which are present in considerable amounts in pilchard oil. On account of their activity both these metals often produce surface- or "skin"-drying.

Among other metals that accelerate drying to a considerable extent, the four metals—lead, cerium, iron and copper—form a class by themselves because of certain characteristic effects they have on gelation and solidification. Although all these metals practically eliminate the inductive period of drying, their accelerative influence on subsequent oxygen absorption and drying is not outstanding. However, they produce a fairly rapid increase in viscosity to the stage where the film is almost semi-solid. After remaining in this state for some time the film solidifies rather abruptly. This phenomenon is especially noticeable with cerium driers. It might appear therefore that these metals exert a peculiar influence on the process of gelation apart from their effect on oxidation but this has not yet been definitely established.

Of the four metals under consideration, only lead and cerium have proven of value as drying catalysts for pilchard oil. As with other drying oils, these metals tend to promote more uniform drying and when used with more active catalysts prevent the rapid solidification of the surface, thus eliminating skin-drying. Copper and iron tend to hasten the disintegration of the dried film, this being especially noticeable in pilchard oil films when copper was used in combination with cobalt or manganese.

None of the remaining metals examined as catalysts showed any pronounced effect on film properties. Antimony, nickel and tin showed a slightly beneficial effect on the hardness of films on aging but not immediately after drying. Contrary to the findings of Rhodes and Chen (1922) the writers found vanadium of little merit as a drying catalyst.

Pilchard oil and other drying fish oils contain more saturated fatty acids than do the drying vegetable oils and this circumstance introduces another way in which the catalyst may affect film properties. When lead, cerium, iron, copper and other metallic soaps of the liquid fatty acids are dissolved in pilchard oil the solutions deposit a precipitate of insoluble soaps after standing for some days. This precipitate consists chiefly of the metallic soaps of myristic,

TABLE I. Influence of various metals on the gain in drying time and weight of pilchard oil

Metal	Hours	Gain in weight %	Metal	Hours	Concentration % as oxide
Co	20	9.0	Co	10	0.08
Mn	24	9.5	Mn	13	0.1
Cu	150	8.8	Pb	30	8.8
Bi	156	9.5	Ce	48	0.13
Fe	156	10.0	Fe	48	0.6
Cd	163	8.4	Al	48	0.17
Pb	186	11.0	Ca	48	0.11
Ce	186	10.0	Sn	48	0.53
Ca	186	11.0	Cu	60	0.04
Mg	188	10.0	U	60	0.14
U	206	11.0	Cd	60	
Sb	210	10.5	Mg	60	0.06
Zn	210	11.0	Sb	60	
Al	216	10.5	Ni	72	0.27
Ni	218	10.5	Cr	72	
Cr	218	10.5	Bi	96	
Sn	226	10.5	Zn	96	0.28
Ba	222		Ba	96	0.04
Hg	223	20.0	Sr	96	0.03
Sr	223	10.5	Hg	120	
			V	120	
Raw oil	400	11.0	Raw oil	267	

Two grams of refrigerated pilchard oil exposed in a glass Petri dish 49.0 mm. diameter constant temperature (25°C.). Drier concentration in each case was 0.03% calculated as oxide of metal. For additional data on these samples see table VI, page 28.

Eight drops of pilchard oil were spread on clean black iron plates 3x3 inches (7.6x7.6 cm.), and plates were exposed in a cabinet at 25°C. Driers prepared originally by dissolving pilchard oil soaps or oxides of various metals, in pilchard oil by heating at 160°C. for two hours.

palmitic, stearic and certain monoethylenic acids. Since lead soaps are much more soluble than those of the other metals this precipitation is more pronounced with this metal. It is well known that lead, copper and iron, especially the oxides, have a marked affinity for fatty oils. Kindscher (1930) suggests that lead oxide (PbO) is capable of saponifying the glycerides to yield lead soaps. In this regard the writers have observed that when a solution of lead linoleate is dissolved in neutral pilchard or other fish oil a precipitate of saturated lead soaps gradually accumulates on standing. It would appear therefore that the saturated fatty acids are split off from the glycerides to precipitate out as lead soaps. It has been suggested also that lead, like mercury, may react with the double bond yielding addition compounds. Both these theories require confirmation.

THE ACTION OF SOLVENTS ON FILMS

The behaviour of films towards solvents throws some light on the film structure. It is well known that drying oil films show greatest affinity for fat solvents and least for solvents that are miscible with water. The behaviour of pilchard oil films towards three types of solvents has been investigated by the writers and the following is a brief summary of the results.

Drying pilchard oil films absorb fat solvents readily and in consequence undergo pronounced swelling. This swelling is greater in the softer interior portion of the film than it is in the more dense surface region. In oven-dried films the surface layer is usually very dense and keratinous;

hence it undergoes very little change in volume. Because of this differential swelling, internal stresses are set up which not only tear the film from its supporting surface but completely disrupt its structure. Furthermore the film substance loses its cohesive and adhesive properties and is easily reduced to a granular residue when pressed or rubbed. If the solvent absorption has not been too extreme and the solvent be permitted to evaporate, it is released almost as rapidly as it was imbibed and the film recovers its normal volume, tensile strength, elasticity and adhesiveness.

Water-miscible solvents such as methyl and ethyl alcohols, acetone, esters, etc., are imbibed less readily by pilchard oil films than are the fat solvents, and swelling is much less pronounced. Prolonged refluxing disrupts the film but does not disintegrate the film polymer to a great extent. The chief effect is the extraction of certain soluble products such as liquid drying components not yet built into the film structure, oxidation products and non-drying glycerides and fatty acids. The drying components of these extractives appear to be a mixture of substances which have reached various stages of polymerization but have not yet reached the gel state. They are gradually built into the film structure and consequently form a progressively smaller proportion of the extractives with aging of the film. In fresh films therefore the extractives consist of a viscous mixture from which the solid constituents crystallize out on standing. In aged films or in oven-dried films, on the other hand, the extracted materials consist mainly of solid white crystalline glycerides and fatty acids along with breakdown products of oxidation. Many oxidation products are relatively hydrophilic in nature and therefore are important because of their influence on permeability of films to moisture. These products increase in amount with aging of films. They are present also in considerable amounts in air-blown oils.

OILS USED

In order to evaluate satisfactorily the drying properties of pilchard oil, three other commercially important oils were used as standards of comparison. These were linseed oil, China wood oil and menhaden oil, of which the characteristics are given in table II.

TABLE II. Characteristics of drying oils

	Iodine val. Wijs 30 min. 0.1500 g. sample	Sap. value	Acid value	Solid F.A. %	Refractive index at 25°C.	Viscosity (Stormer) 25°C.	Drying time (hours)
Pilchard....	180.0	169.5	1.5	21.3	1.4810	52.2 cp.	269
Menhaden..	172.1	167.7	9.0	13.6	1.4795	48.7 cp.	269
Linseed....	184.9	168.9	2.4	6.7	1.4800	47.9 cp.	293
China wood.	150.7	168.9	5.2	68.3	1.5164	178.5 cp.	72

Characteristics of solid fatty acids
(Baughman and Jamieson's method)

	Iodine value	Neut. value	Melting point °C.
Pilchard.....	3.2	268.4	53
Menhaden.....	5.9	270.5	53
Linseed.....	1.5	302.4	51
China wood.....	135.8	295.8	33.5

The linseed oil was washed repeatedly with hot water to remove any natural anticatalysts, then dried over anhydrous sodium sulphate and stored under carbon dioxide. Wintered men-

haden oil was used but its history and temperature of destearinization were not obtainable. The pilchard oil sample was refrigerated at 6° C., which temperature is recommended for destearinization when this oil is to be used for protective coatings.

The solid fatty acid content of raw pilchard oil and menhaden oil is practically the same for both and varies from 22 to 24 per cent. The difference shown in the above table is due to difference in the degree of destearinization. China wood oil yields a large proportion of solid fatty acids but these consist chiefly of solid unsaturated components—mainly β -elaeostearic acid.

SOFTNESS AND TACKINESS OF FILMS

Although pilchard oil dries more rapidly than linseed oil, its films are somewhat inferior in hardness and tensile strength. These qualities largely determine the property of toughness which is essential to any protective coating. On the other hand, pilchard oil films possess superior flexibility and stretching capacity, properties necessary in films subject to expansion and contraction or to folding. Thus, while it is desirable to improve the hardness and toughness of pilchard oil films it is equally desirable to retain their normal flexibility and distensibility. These two sets of properties in any film are complementary to each other, and unfortunately it is practically impossible to improve the one without adversely affecting the other. Any treatment, therefore, that improves hardness usually detracts from distensibility.

Another defect, always associated with softness in drying oil films, and one which is very characteristic of fish oil films, is tackiness. This quality is present in greater or less degree in all films made from raw drying oils but in linseed and China wood oil films it is relatively slight and may be eliminated almost entirely by the use of driers. In fish oil films it is much more pronounced and persists to an objectionable degree even when driers are used. These films, therefore, collect dust rapidly and become dull.

Softness and tackiness have a common origin in incompleteness of film structure. This deficiency in turn arises from the presence of excessive amounts of components which do not dry and hence do not contribute to the actual film network. Their presence, therefore, interferes with the linking up of components that do dry. Thus, in soft films, because of incomplete polymerization, the film network is relatively open. Such a structure possesses flexibility and stretching capacity but lacks tensile strength and toughness. Also, properties such as permeability and the capacity to absorb liquids and gases, are accentuated. Tackiness in these films no doubt arises from the presence of semi-liquid components and from the attractive forces of free active groups such as unsaturated bonds and polar groups of the partly polymerized molecules. Harder films, on the contrary, possess a more complete and compact structure, freer from interfering substances and with fewer free active groups exposed; consequently, tackiness and capillary properties are much reduced. It is evident, therefore, that any treatment that improves hardness of films also tends to reduce tackiness.

Chief among the components that interfere with proper drying of fish oil films are the glycerides that contain a preponderance of non-drying saturated and monoethylenic fatty acids. In addition to these, there are glycerides containing both drying and non-drying fatty acids. Of this group only those glycerides

which contain a preponderance of drying members can contribute towards the film structure. In any case the presence of non-drying fatty acids is a detriment. It is the liquid or semi-solid monoethylenic fatty acids among these that are largely responsible for tackiness. This can be shown easily by adding a non-drying oil such as olive or cottonseed oil (which contains a large proportion of monoethylenic fatty acids) to linseed oil and noting the increased softness and stickiness of the dry film. Solid glycerides, such as beef suet, when added to linseed oil in this manner, do not impart tackiness but yield a film that is dull, smooth and waxy. To improve pilchard oil films, therefore, it is necessary to remove the interfering non-drying components. When this is done, as for example by steam treatment (see paper No. IV in this series), tackiness of films disappears and hardness is increased many hundred per cent.

Hardness in films fluctuates, depending on conditions of temperature, humidity and illumination. Fish oil films, if kept in a desiccator for a few hours, become harder and quite free from tackiness. Upon removal, they revert within a few seconds to their former state. If the film surface is rubbed twice with the finger, the increase in tackiness, due to increased temperature and disturbance of surface structure, is very noticeable the second time. Both increased temperature and humidity diminish hardness and increase tackiness. Doubtless this is brought about to some extent by the softening of certain of the solid constituents of the film, but there is evidence also of some sort of temporary and slight dissociation of the film structure with release of certain attractive groups that tend to impart tackiness. These changes are reversible, the process of association apparently being much slower than that of dissociation.

Light also has an influence on hardness and tackiness. Films dried in the dark are usually softer and tackier, especially a few days after solidification is complete. If then exposed to light they gradually become harder and less tacky. This effect varies with the wave-length of the light. It is greatest with the ultra-violet and diminishes towards the red. The influence of light will be discussed further in connection with the yellowing of films (page 36). It is sufficient to mention that when films become softer after removal from the light, the change is usually accompanied by yellowing.

METHOD OF MEASURING HARDNESS

The apparatus used for estimating hardness of films consists of an ordinary triple-beam laboratory scale provided with a sturdy upright rod supporting an adjustable arm. The arm is provided with an insulated steel pin which just touches the centre of the platform when the weights are at zero. The pin is 1 mm. in diameter and rounded evenly and smoothly at the tip. The platform and pin are connected in series with an electric buzzer and battery so that when the pin touches the metal platform, the buzzer is activated.

Films for hardness tests were prepared on carefully cleaned black iron plates 3x3 inches (76x76 mm.). Eight drops of oil sample from a pipette (eye dropper) were spread on the plate with the finger, first in one direction and then the other. By spreading twice in each direction, an even distribution of oil was obtained, the amount of oil lost by adhering to the finger being approximately the same in each case. The coated plates were then placed on a level sheet of plate glass in a ventilated oven maintained at 25°C., until dry. Films made by this method did not vary considerably in thickness from one plate to another. The thickness was approximately 0.08 mm.

To determine the hardness of a film the plate was placed on the platform with the pin just touching the film surface. The weights were then adjusted to an estimated position and the scale arm released carefully so that any sudden increase in pressure of the pin upon the film was avoided. After two or three trials, changing the position of the plate each time, the correct position of the weights could be determined. The weight in grams required to puncture the film five seconds after release of the scale arm was taken as a measure of the hardness. In practice the average of several determinations was usually taken, the number depending on the variability of the results. Some films, due to the driers used, displayed a marked tendency to crawling or cissing, thus producing great variation in thickness of the films. In such cases the only alternative was to select points where the film appeared to be of ordinary thickness and to take the average of a large number of determinations. In all determinations the weight of the plate was deducted.

The puncture method of estimating hardness has been chosen because it simultaneously combines a measure of toughness, tensile strength and adhesiveness. An improvement in any of these properties results in greater resistance to puncture.

METHODS OF IMPROVING HARDNESS IN FILMS

Use of driers. The superior merit of cobalt as a drier for pilchard oil has already been discussed. In table III is given a comparison of the hardness of films containing various driers. Most of the drier solutions were made by dissolving pilchard-oil soaps of the various metals, in pilchard oil by heating at 160°C. for two hours.

TABLE III. Relative hardness of pilchard oil films containing various driers

	gm.		gm.
Cobalt soaps.....	42	Strontium soaps.....	42
Manganese soaps.....	42	Magnesium soaps.....	37
Lead soaps.....	42	Mercury soaps.....	32
Lead oxide.....	62	Antimony.....	62
Cerium soaps.....	62	Bismuth.....	42
Copper soaps.....	42	Vanadium.....	27
Iron soaps.....	62	Tin.....	72
Aluminium soaps.....	37	Lithium.....	42
Nickel soaps.....	67	Cobalt acetate.....	52
Chromium soaps.....	42	Cobalt resinate.....	67
Uranium soaps.....	42	Cerium resinate.....	72
Cadmium soaps.....	37	Cobalt—cerium.....	92
Zinc soaps.....	42	Cobalt—lead.....	22
Calcium soaps.....	42	Ferrous sulphate.....	82
Barium soaps.....	42	Cobalt linoleate.....	72

The data in table III represent averages of the results of tests on duplicate samples. In general when duplicates or larger numbers are plated at the same time and dried under identical conditions they give closely agreeing results. The order in one series of tests will usually differ somewhat from the order in another, even when films are dried under uniform conditions of temperature humidity and illumination. The variations in order occur chiefly in films that give nearly equal hardness values. It is likely that these differences arise largely from changes occurring in the sample between tests, or in variations in the surface

of the iron plates, or possibly in slight variations in conditions of drying. For example, samples, if not protected, may become oxidized, take up moisture, or the physical state of the dissolved catalyst may change. Very slight variations in any of these factors may account for film variations. It is very difficult, therefore, to determine precisely the relative merits of various metallic driers by simple physical tests. This information will come only through fundamental studies on the mechanism and rates of catalysis, and the physico-chemical changes in film structure during drying.

Table IV illustrates the change that occurs in hardness of films subsequent to drying. The films tested were kept in a dark cabinet at 25°C. and constant humidity throughout the entire test.

It is seen that some films reach a maximal hardness within a day or two after drying. The period of increasing hardness varies with the oil, the treatment to which it has been subjected, and on conditions of drying. As mentioned before the diminution in hardness generally accompanies the onset of yellowing.

While resinates and tungates of various metals tend to improve hardness in films, they introduce or accentuate other undesirable qualities. Thus, resinates promote "cissing" or the tendency of liquid films to "gather" or become "unspread" during drying. Tungates accentuate the tendency of films to wrinkle and turn yellow in the dark. Furthermore, because of their relative insolubility they precipitate out more readily and impart a dullness to films. Exposure tests have demonstrated that neither tungates nor resinates have any special merit from the standpoint of their influence on durability of films.

TABLE IV. Increase in hardness of various samples on drying at 25°C.

	Hours									
	1	2	3	4	7	10	20	35	70	190
Refrigerated pilchard oil										
+cobalt.....	..	Dry	22	37	52	72	82	122	117	121
+lead.....	..	..	..	..	..	..	..	..	67	102
bodied+cobalt.....	..	..	Dry	12	22	22	42	47	67	62
air-blown+cobalt.....	..	Dry	27	48	62	77	97	117	112	112
bodied + Amberol gum + cobalt.....	..	..	Dry	32	72	72	97	127	137	172
steam-bodied + cobalt dis- solved in turpentine.....	Dry	72	230	430	..	over 2000	..	..	over 7000	..
steam-bodied (slightly less) +cobalt in carbon tetra- chloride.....	..	..	Dry	7	7	20	32	72	162	382
Linseed oil										
+cobalt.....	..	..	..	..	..	42	92	197	232	192
China wood oil	..	..	..	Dry—films discarded because of wrinkling. Hardness over 2000.						
+cobalt.....										

(Hardness measured in terms of grams weight necessary to puncture the film).

Sulphur dioxide treatment. In the course of a study of the influence of sulphur and its compounds on the film properties of pilchard oil it was found

that simple treatment of certain samples of the oil with dry sulphur dioxide in the dark increased the rate of drying and hardness of films. Surface film formation occurred about two hours earlier than normally, but the actual time required for complete solidification was not greatly reduced. The hardness of the resulting films was about twice that of films from untreated samples. In addition, tackiness and yellowing were completely eliminated. Oven-dried films from these samples were very dark in colour and leathery in appearance and to the touch. They were stiffer and more easily cracked on bending. Exposure tests on films of sulphur-dioxide-treated oil showed that the films were only about two-thirds as durable as those from untreated oils.

Subsequent experiments showed that sulphur dioxide was effective in improving hardness only when applied to strictly fresh pilchard oil. If the oil was the least bit oxidized or rancid no improvement in hardness of the films was noted. In view of this circumstance and the more rapid disintegration of the films of sulphur-dioxide-treated oils, the method is of little value. It may, however, have some value in the treatment of oils for interior finishes.

Treatment with super-heated steam. Steam-bodding is the most effective means of overcoming the natural defects of pilchard oil films. The details of this process have been described in a previous publication (Brocklesby and Denstedt 1934). The end-product of this treatment (when thinned with a suitable solvent) dries very rapidly with the aid of a small quantity of soluble cobalt drier. The resulting films are free from all the defects of ordinary films. They are glossy and absolutely free from tackiness. Furthermore, they possess very low permeability to moisture and are practically free from the tendency to turn yellow in the dark. In appearance they are like varnish films in gloss and evenness of surface.

Figure 4a shows a section of a film from a steam-bodied oil about one millimetre in thickness. The surface layer is extremely hard and shows conchoidal fracture when cut or broken. Some of the solid components still remain in the inner part of the film but these never diffuse through the dense, keratin-like surface layer. Hence these films do not bloom.

Oven drying and baking of films. This method of improving hardness and reducing tackiness in films is obviously of limited application. However, because of the long recognized merit of fish oils in baked finishes for metals the question of oven treatment warrants some attention.

The influence of oven treatment on hardness is illustrated in table V.

TABLE V. Influence of heat treatment at 100°C. on hardness of films

Oil	*Original hardness	—After heating at 100°C. for—		
		30 min.	60 min.	90 min.
Raw pilchard oil.....	66	87	over 3000	
Raw menhaden oil.....	40	57	57	over 3000
Raw linseed oil.....	500	530	1700	over 3000
Steam polymerized pilchard oil.....		1900	over 3000	

*Films were kept three weeks at ordinary temperature before testing.

Oven-drying simulates air-blowing in that the oil is oxidized more rapidly at higher temperatures and the volatile components are driven off. Polymerization, therefore, takes place more completely, and consequently the film structure is more compact. Even at temperatures as low as 60°C. pilchard oil films dry hard and completely free from tackiness. At higher temperatures hardness is greatly increased and at the same time the weight is diminished from loss of volatile material. This loss is somewhat compensated by an increase in weight due to absorption of oxygen. Table VI illustrates the "apparent" gain or loss of weight of pilchard oil samples containing various driers. Duplicate samples—2 grams in each case—were weighed accurately in small Petri dishes 49 mm. in diameter and dried at 160°C.

TABLE VI. Percentage changes in weight of dry samples on oven treatment at 160°C. and subsequent exposure to moisture

	1. After oven treatment for 12 hours	2. After oven treatment for 36 hours	3. After exposure to moisture saturated air at 25°C. for 50 hours (Gain)	4. After oven treatment for 27 hours (Loss)
Mg.....	-7.7	-8.5	1.38	-2.89
U.....	-8.5	-9.1	1.24	-3.02
Ni.....	-8.4	-9.2	1.19	-2.90
Pb.....	-8.5	-9.3	1.23	-2.89
Cu.....	-8.0	-9.2	1.12	-3.21
Co.....	-6.6	-7.4	1.20	-2.80
Zn.....	+5.2	-9.1	1.13	-2.73
Sr.....	-8.5	-9.4	1.23	-2.92
Fe.....	-9.7	-8.0	1.20	-2.78
Mn.....	-7.6	-8.6	1.27	-3.24
Ca.....	-8.2	-8.9	1.25	-2.72
Ce.....	-8.2	-9.1	1.17	-2.64
Al.....	-8.6	-9.5	1.11	-2.51
Sn.....	-8.8	-9.7	1.09	-2.48
Sb.....	-8.0	-9.0	1.22	-2.63
Hg.....	-8.3	-9.2	1.24	-2.64
Cd.....	-8.4	-9.5	1.19	-2.37
Bi.....	-8.2	-10.8	1.15	-2.46
Raw pilchard.....	-9.0	-9.9	1.06	-2.37
Raw linseed.....	+0.26	-0.89	0.70	-1.18
Raw China wood.....	+0.96	+0.65	0.49	-1.07
Raw menhaden.....	-5.7	-7.0	1.04	-2.11

Note—Percentage for (1) and (2) based on weight of the solid film at the start, (3) based on weight of film after (2) and (4) based on weight of film after (3).

It will be observed that the second oven treatment produces a loss in weight much in excess of the increase due to moisture absorption. Moisture treatment therefore assists the escape of volatile products.

The relatively smaller loss during the first two periods in the case of cobalt and manganese is presumably due to greater oxygen absorption. Similarly, the more rapid oxygen uptake of pilchard oil explains the difference between the

behaviour of the pilchard oil samples and those of linseed and China wood oils.

Oven treatment of pilchard oil films (containing driers) either during or after drying, produces a marked darkening of colour. At 160°C ., for example, the colour changes from pale straw to brownish red within a few hours. Menhaden oil films behave in the same manner, but linseed and China wood oil films undergo comparatively little change in colour. Pilchard oil films without driers, on the other hand, do not change considerably in colour at 160°C . Driers, therefore, bring about extensive oxidative splitting of the fatty acids with the formation of dark coloured products, which are probably formed by condensation after disruption.

Another defect that appears after oven treatment of pilchard oil films is "blooming" or the gradual accumulation of crystalline solid fatty acids and glycerides on the film surface to produce a dull whitish coating. This will be discussed in detail later. Films dried at moderate temperatures show blooming the most. At higher temperatures more of the saturated fatty acids are driven off and consequently blooming is less pronounced.

Other methods of improving hardness. The compounding of pilchard oil with linseed oil or China wood oil, the use of so-called "hardeners" such as ferrous sulphate, lime, etc., and the incorporation of various gums, have all been investigated as means of improving hardness of pilchard oil films. Blended products simply combine the merits and defects of the oils used. Hardeners have only a slight influence on freshly prepared films but their effect becomes more marked with aging of the film. Gums, properly cooked into pilchard oil, improve hardness but tend to promote cissing and yellowing. Furthermore, they tend to make films brittle on aging.

PERMEABILITY AND MOISTURE ABSORPTION OF FILMS

All drying oil films, because of their sponge-like structure, absorb and transmit moisture. This capacity varies with the number and size of the film capillaries and therefore diminishes with increased density or compactness of the film. It may be inferred then that ordinary fish-oil films are more permeable to moisture and gases than linseed oil films, notwithstanding the statements often found in the literature to the contrary.

Permeability and moisture absorption have long been recognized as having a direct influence on the durability of coatings. It is well known, for example, that paint coatings deteriorate rapidly in localities along the sea-coast where rainfall is excessive. Experiments have shown, too, that soft films with a high capacity for absorbing water are the first ones to break down.

SWELLING

The mechanism by which moisture promotes disintegration of films is complex. Doubtless there is a certain degree of hydrolysis which, though extremely slow, becomes considerable over a long period. Also it is not impossible that excessive moisture may bring about a degree of decomposition of some polymerized components of the films. These chemical effects of moisture, however, are insignificant compared with the physical effects. It has been pointed out

before that films swell when they take up moisture and that swelling is greater in the soft interior of the film than in the more compact surface layer. Swelling, then, has two destructive effects: (1) it tends to detach the film from the surface to which it adhered, and (2) the differential swelling tends to destroy the integrity of the coating. The breakdown of films from swelling occurs quite rapidly where moisture is extreme. Under more moderate moisture conditions, however, so long as moisture can escape from one side of the film as rapidly as it is absorbed at the other, very little swelling occurs.

The following experiment will illustrate the behaviour of ordinary pilchard films on exposure to excessive moisture. A galvanized-iron sheet was given three

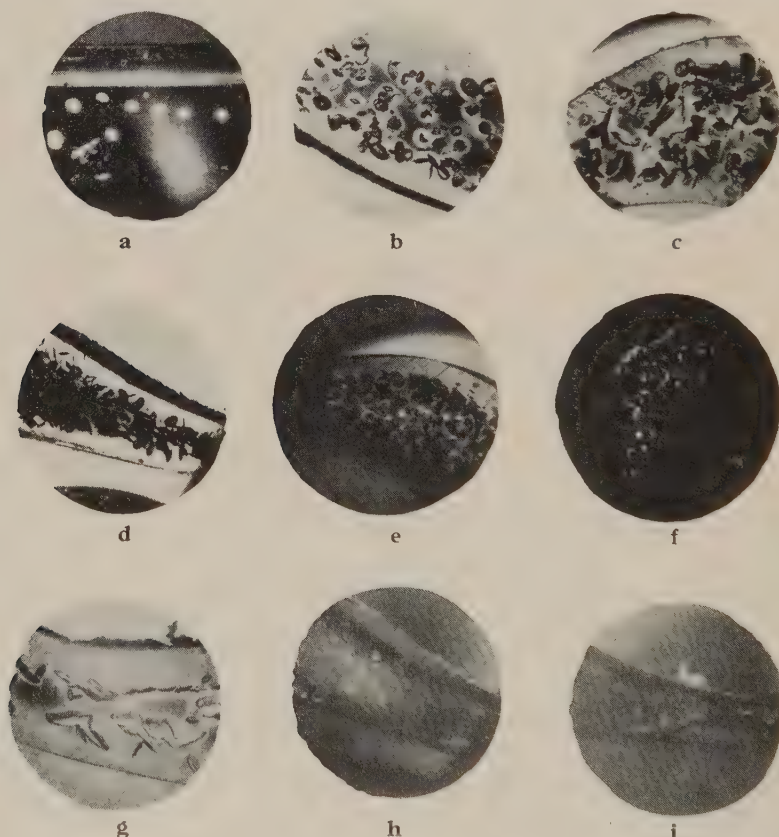


FIGURE 4. **a**,—Film from steam-bodied oil (thickness about 1 mm.) under crossed nicols **b** and **c**,—Pilchard oil film partly dried after saturation with moisture. Note the cavities and opacity in the inner layer. Uncrossed nicols. **d**,—Pilchard oil film completely saturated with moisture. **e**,—Pilchard oil film containing moisture as viewed through partly crossed nicols. **f**,—Film viewed through fully crossed nicols showing crystal linings of cavities. **g**,—Section of a pilchard oil film which had been saturated with moisture and then placed in boiling water for one minute. **h**,—The formation of crystalline bloom on the surface of the film as viewed through crossed nicols. (Film had been exposed to excessive moisture). **i**,—Similar film viewed through partly crossed nicols.

coats of brown pilchard-oil paint and allowed to remain in a desiccator for several days. It was then cut into two panels 4x7 inches (10.2x17.8 cm.) which were designated as A and B respectively. Panel A was placed in a moisture cabinet saturated at 25°C. After 12 hours' exposure not only had the film become extensively wrinkled but it had lost its adhesiveness and in expanding had slid along the plate in all directions from the centre, so as to hang over the edges of the plate to the extent of about 2 per cent. of its dimensions. Allowing for wrinkling, the estimated expansion of the film was roughly 5 per cent. The plate was then placed in an oven at 60°C. for six hours. Within five minutes the film shrank to dimensions about 2 per cent. less than those of the plate, and its surface was free of wrinkles. During the remainder of the period there was no further measurable contraction. To see if the film would again expand in the presence of moisture, the plate was returned to the cabinet for 12 hours. This time there was a much smaller degree of wrinkling and practically no extension. Presumably the film during the preceding period in the oven had become more compact in structure, and consequently its permeability and swelling capacity were diminished. Except for the wrinkled portions, the film this time maintained its adhesion to the metal.

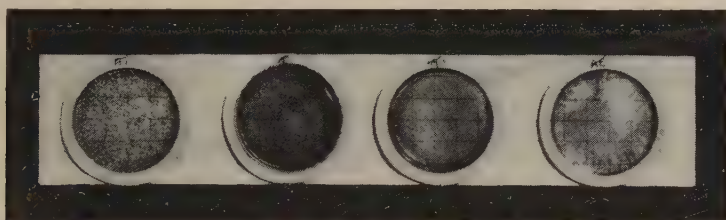


FIGURE 5. Film membranes for permeability and moisture absorption tests.

Plate B, on the other hand, was placed first in the oven. At the end of 12 hours the film had become shrunken and showed definite checking and cracking. On being transferred to the moisture cabinet it became slightly wrinkled but still maintained its adhesion.

Films, on absorbing moisture, gradually become non-transparent and dull due to the adsorption and condensation of water on the walls of the capillaries in the less compact portions of the film. This phenomenon, one type of "bloom", is usually detectable when the moisture content is about 5 per cent., and transparency is lost when the content reaches about 5.5 per cent. It has already been pointed out that this phenomenon is confined to the inner softer portion of the film, the surface layer remaining transparent even after completely saturating the film by immersing it in water for prolonged periods. The photomicrographs given in figure 4, b to g, show the distribution of bloom in moisture-saturated pilchard and linseed-oil films. It is illustrated best in photograph b by the shaded areas between the cavities.

It is interesting to note in figure 4b that the gel immediately surrounding the solid masses in the pilchard oil films retains its transparency, thus indicating a

greater density. When viewed through crossed nicols as in figure 4, e and f, the lining of the cavities containing the solids appears to be covered with crystals which sparkle with brilliancy.

MEASUREMENT OF ABSORPTION AND PERMEABILITY

I. ABSORPTION

Many methods for measuring permeability of oil films are described in the literature but all are open to criticism, chiefly because of the difficulty in obtaining

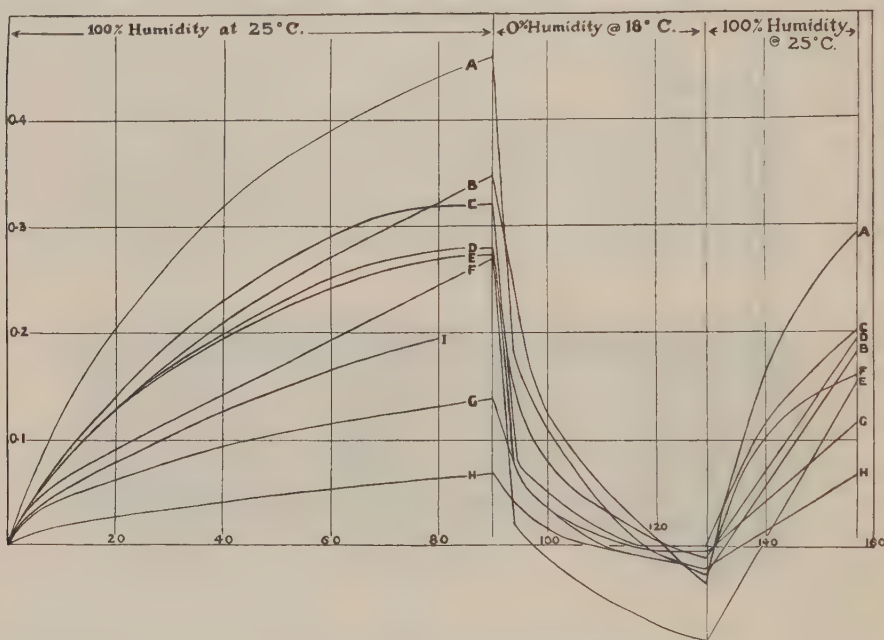


FIGURE 6. Moisture absorption of solid films. A,—Pilchard oil treated with sulphur dioxide. B,—Raw pilchard oil with cobalt drier. C,—Raw linseed oil with cobalt drier (wrinkled). D,—Pilchard oil blown with air at 160°C. E,—Wintered menhaden oil with cobalt drier. F,—Bodied pilchard oil+gum. G,—Bodied pilchard oil. H,—Steam-distilled bodied pilchard oil. I,—Linseed oil (non-wrinkled) very slightly bodied.

uniformity of film weight and thickness. The method finally adopted by the writers may be considered a modification of that used by Muckenfuss (1913, 1914), who followed the increase in weight of a dish of calcium chloride, separated from a moisture-saturated atmosphere by an oil film dried on filter paper. By this means Muckenfuss was able to compare quite satisfactorily the permeabilities of linseed oil, China wood oil, menhaden oil, and others. On trying this method, however, the writers experienced considerable difficulty in preparing uniform films. The method of film preparation, therefore, was modified as described below so as to obtain films of equal area and thickness.

Film preparation. An ordinary fruit-jar rubber ring (outside diameter, 76 mm., inside 61 mm.) was cemented to a perfectly flat XXX tinned-iron plate (24 gauge). The surface of the plate

within the ring was then amalgamated slightly with mercury and exactly three grams of oil were introduced within the ring. The plate was then placed on a levelled tray in a cabinet maintained at 25°C. to dry. After a few weeks when the film had solidified throughout, the outer edge of the ring was detached from the plate and the latter was immersed in mercury. In an hour or so the mercury worked its way into the inner amalgamated area, thus releasing the film. The underside of the film usually is not thoroughly dry and therefore it is advisable to place the film in the cabinet again on mercury, underside up, for a few days. A few specimens of membranes are illustrated in figure 5.

Films prepared by this method are as a rule uniform in thickness except for a slight meniscus at the ring. Most important of all is the ease with which any membrane can be duplicated. Some films are difficult to prepare free from wrinkles. This, of course, would increase the rate

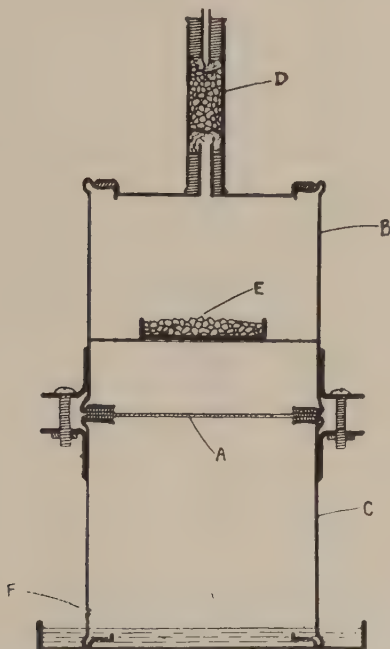


FIGURE 7. Device for measuring permeability of films to moisture.

of moisture absorption, owing to the greater surface area exposed. It is necessary therefore to prepare additional films, using smaller amounts of drier. It is almost impossible to prepare films of China wood oil in this manner free from wrinkling without first bodying the oil.

Rate of Moisture Absorption

To determine the rate of absorption of moisture, film membranes such as described above, were suspended in a moisture-saturated atmosphere maintained at 25°C. Ample space was left between the samples and both the water and the air in the cabinet were kept in constant agitation. Six rubber rings were also included in the experiment as controls. All samples were weighed accurately at the start and at intervals during the exposure.

The relative rates of absorption of various films are indicated in figure 6. The films were exposed to moisture for 90 hours. After that time they were removed and placed in a desiccator over calcium chloride at 18°C. and again weighed periodically for a period of 39 hours. They were then again placed in

the moisture cabinet for another period of 29 hours, during which time they were weighed four times.

The curves reveal some interesting details. Ordinary fish-oil films not only absorb moisture more rapidly than linseed-oil films but they possess a remarkable capacity for moisture. In some experiments where the films were exposed to moisture for a very long time (160 hours) some of the fish-oil films absorbed up to 50 per cent. of their weight of water. Under such conditions the surface layer of the menhaden-oil film and also that of the blown pilchard-oil film began to revert to the original fluid state. It is evident from the graphs that blowing increases the proportion of hydrophilic substances in the film. Steam distillation, on the other hand, greatly reduces the moisture absorption; so also does the incorporation of gums. The influence of wrinkling of the film on the moisture absorption is shown by a comparison of the two linseed oil films. The non-wrinkled film was prepared from an oil which had been slightly bodied and the lower absorption may perhaps be due in part to this treatment.

With regard to the rate of loss of moisture on removal of the films from the moisture cabinet it will be observed that all the curves go below the origin, indicating that the films themselves have lost weight in addition to the water given off. This loss of substance possibly leaves the films more porous than the original and thus may explain the more rapid uptake of moisture during the second exposure. Since each successive drying and exposure to moisture increases the moisture-absorbing capacity of any film, it is readily understood why films exposed to excessive moisture disintegrate so rapidly.

II. PERMEABILITY

The apparatus used for determining the rate of moisture transmission through the film is illustrated in figure 7.

The membrane A, with a rubber ring on either side, was clamped between two half-pint tin canisters, B and C (75 mm. deep x 75 mm. diameter), the bottoms of which had been cut out so as to leave a narrow flange around the circumference. The cover of the upper can was provided with a tube (D) containing Desicchlora A (Baker's anhydrous barium perchlorate) and was fitted with a rubber ring to prevent any passage of air around the edge. E represents a small petri dish supported by a coarse galvanized screen and containing a known weight (about 8 grams) of Desicchlora. A small perforation was made about 2 cm. from the mouth of the lower can at F to permit equalization of pressure. The apparatus when assembled was placed in a petri dish containing water, in a cabinet maintained at the desired temperature. The dish of Desicchlora was weighed periodically and during weighings was kept covered.

Figure 8 shows the results of a permeability test carried out at three temperature levels. It will be observed that permeability is linear at any temperature but that the rate of transmission is not always strictly proportional to the temperature. For example, the rate in the case of the air-blown pilchard-oil film was less than that of the menhaden oil film up to 30°C. but greater at 40°C. On the contrary the increase in rate at 40°C. in the case of the steam polymerized pilchard-oil film is not as great as expected from the comparison of the rates at 25°C. and 30°C. These variations illustrate very well how treatment affects the nature of the film structure and the difference in response of these films to temperature changes.

Both the absorption and permeability experiments show that the capacity of a film to take up and transmit moisture is increased whenever the proportion of water-soluble or polar constituents is increased, as for example by blowing with air or by sulphur-dioxide treatment. Films are more permeable also when slow driers are used, presumably because of the looser film structure. Rapid driers like cobalt, on the other hand, tend to reduce permeability. The most effective treatment for reducing permeability, however, is steam distillation. It is true that the hydroxyl content of the oil is increased by this treatment but any increase in permeability due to these groups is far outweighed by the counter-effect of polymerizing the oil and removing the bulk of non-drying components. In addition, the swelling coefficient of films is greatly diminished. The incorporation of gums in pilchard oil tends to make films less permeable but not to any great degree.

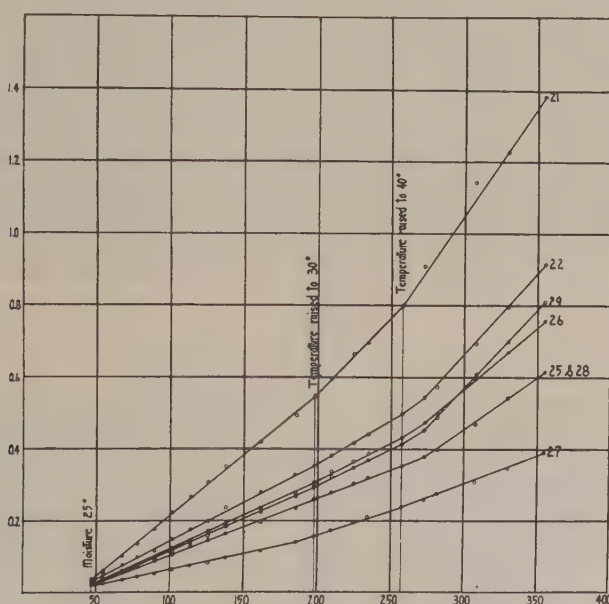


FIGURE 8. Permeability of films to moisture. 21,—Pilchard oil+cobalt. 22,—Linseed oil+cobalt. 25,—Pilchard oil containing rosin+cobalt. 26,—Menhaden oil+cobalt. 27,—Steam-bodied pilchard oil+cobalt. 28,—Steam-bodied pilchard oil+cobalt (less body). 29,—Air-blown pilchard+cobalt.

YELLOWING OF FILMS

All drying oil films tend to become yellow or brown when kept away from direct light. China wood oil films are notorious for this defect while poppy seed oil films are practically free from it. Linseed oil and fish oil films lie between these extremes, the latter approaching China wood films in yellowing tendency.

Numerous theories have been advanced to account for yellowing. Until recent years it was attributed to various causes, as for example, the action of ammonia of the atmosphere, changes in the natural pigments in the oils, and to the influence of driers and mineral pigments in paints. It is now known that some of these may catalyse the chemical change giving rise to yellowing,

but the change occurs in the film substance itself. That a change in the natural pigments in oils is not the cause of yellowing has been shown from the circumstance that decolourization of oils does not eliminate the defect. On the contrary, removal of the pigments from pilchard oil accentuates yellowing of films. Werthan and colleagues (1930) have demonstrated the influence of heat, humidity, driers and pigments on the yellowing of white paints. They have shown also the influence of light of various wave lengths on the production and elimination of yellowing. Thus the longer wave lengths promote yellowing whilst the short wave lengths inhibit it. Similar findings of the writers are described later.

The chemical nature of yellowing is still obscure. However, as Milas (1932) points out, chiefly two theories are current. Morrell and Marks (1931), on the one hand, suggest that the phenomenon is attributable to keto-enol transformations of certain oxide groups with the formation of coloured salts in the presence of bases. Elm (1931, 1932), on the other hand, attributes it to under-polymerization of certain polyketones formed during oxidation of the oil. Milas suggests also that yellowing may be due to slow oxidation and polymerization of aldehydes. In the opinion of the writers the phototropic phenomenon of yellowing is due to a tautomerism, the colourless form being produced by the energy absorbed from light of short wave-lengths. In the absence of short waves the less stable form loses energy and reverts to the coloured form. The change from the colourless to the coloured form is accompanied by an alteration in the structure of the film, the latter becoming softer as yellowing proceeds. Whilst our present knowledge of yellowing is still very indefinite, it is generally agreed that it involves intermediate oxidation products and that it is apparently accelerated by moisture, certain driers, pigments and the absence of short-wave radiations.

Figure 9a illustrates the influence of light of different wave lengths on the yellowing of white paint made from pilchard oil, white lead and zinc oxide. A metal panel was given three coats of the paint, each coat being allowed to dry thoroughly in the sun for several days. Small square coloured-glass filters were then laid on the panel and the latter exposed to direct daylight every day for a month.

Figure 9b illustrates the bleaching influence of sunlight on a pilchard oil film, parts 1 and 2 of which had been covered with brown cardboard for a period of two years. The film was prepared originally by impregnating heavy filter paper with refrigerated raw pilchard oil. At the end of the period, part of the covered area (centre) was exposed for four days. The area to the right was left exposed to ordinary light during the entire period. This shows that prolongation of the yellow state does not make the chemical groups, which are responsible for yellowing, any more stable to light. Yellowing develops rapidly and reaches a maximum intensity in a few weeks.—about six weeks in the case of the above film. It is noteworthy that certain white paints made from sulphur-dioxide-treated pilchard oil and which did not spontaneously turn yellow in the dark, became yellow when covered with red glass and exposed to sunlight for a week. These yellowed portions remained yellow when kept in the dark but were readily bleached again by light.

CORRECTION OF YELLOWING

When refrigerated raw pilchard oil is used for protective-coating purposes, cobalt driers give slightly less yellowing than manganese, lead and others. The incorporation of benzoyl peroxide is also slightly beneficial.

Sulphur-dioxide Treatment

This treatment, described before, is very effective in preventing yellowing provided it is applied to a relatively non-rancid oil. White paints made from oil so treated have retained their whiteness and hardness after being kept in the dark for three years.

Steam Polymerization

Blowing refrigerated oil with steam at about 300°C., as previously described, is the most effective means of eliminating the natural defects of pilchard oil films, including yellowing. White enamels made from steam-blown products have been found to retain their whiteness.

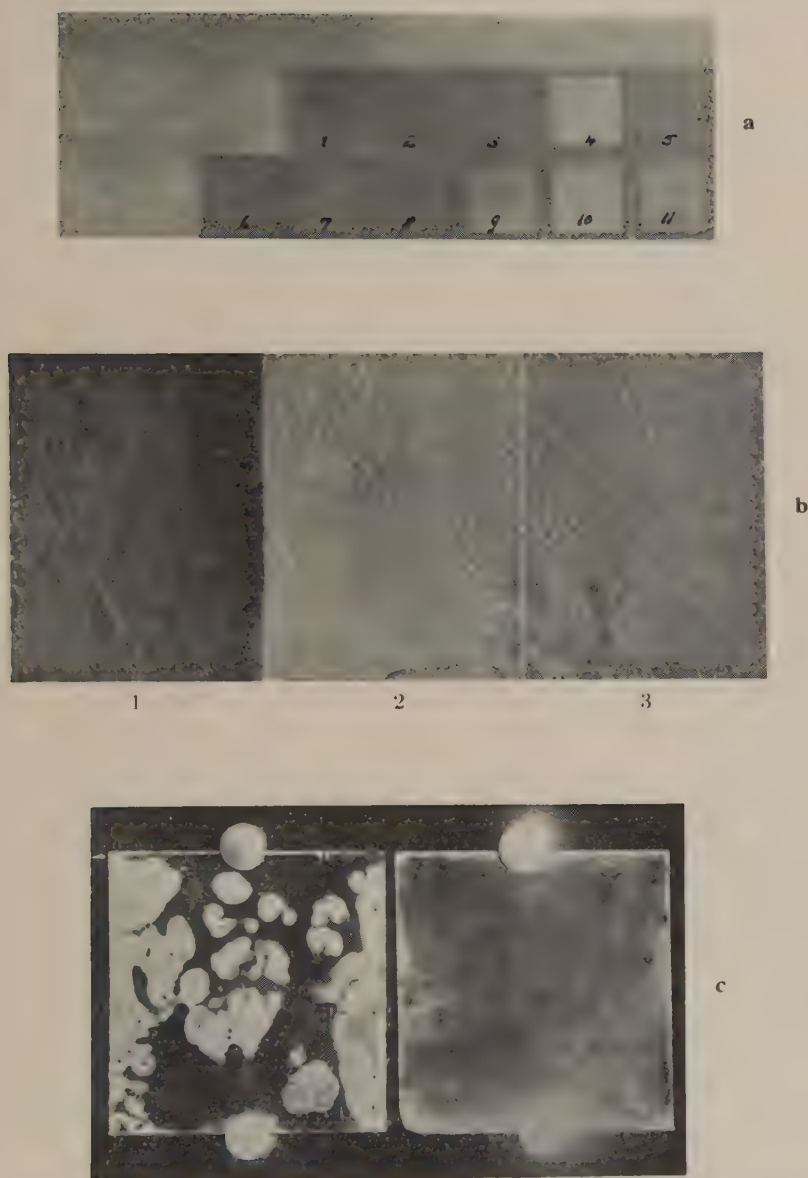


FIGURE 9. **a**,—Yellowing produced in white paint by covering part of the surface with coloured glass filters and exposing to sunlight. Transmission ($\text{cm} \times 10^{-5}$): 1,—red celluloid; 2,—red filter, 600 up; 3,—red filter, 600 up; 4,—pink filter, 400-460, 550 up; 5,—orange filter, 560 up; 6,—deep yellow, 535 up; 7,—light yellow, 605 up; 8,—deep green, 500-570; 9,—light green, 400 up; 10,—deep blue, 410-510; 11,—very pale yellow, 400-500, dim, 500 up, bright. **b**,—Bleaching of yellow film by light. 1,—covered for two years; 2,—same as (1) but bleached by light within four days' exposure to daylight; 3,—portion left exposed to light during the entire period. **c**,—Cissing in pilchard oil film (left) and correction of the defect by means of lead drier (right).

Whether the inhibition of yellowing is attributable to the extreme degree of polymerization effected by the processing or to the removal of certain components of the oil, is difficult to say. That the polymerization instead of the oxidation of certain unsaturated linkages is a probable explanation is supported by the finding that yellowing is always much slower and less pronounced in films made from oils bodied *in vacuo*. On the other hand, it will be recalled that yellowing is pronounced in films from air-blown oils. Furthermore, certain of the unpolymerized distillate fractions from steam distillation show a tendency to become yellow on standing exposed to air. There is no doubt that polymerization tends to eliminate this phenomenon.

CISSING

This phenomenon may occur in any drying oil film under certain conditions. It is characterized by the failure of films to remain spread. Such films, an hour or so after application, usually collect into numerous pools, apparently leaving the intervening patches of the supporting surface exposed. The defect rarely occurs in paint films, because the pigments by their capillary action tend to prevent recession of the oil. In oil films, however, especially in drying fish oil films containing certain driers and solvents, it occurs very frequently. Experiments have shown that among the metals conducive to cissing are manganese, iron, mercury, calcium, magnesium, vanadium and many others. Those with a less pronounced tendency are cobalt and copper. Lead and cerium driers on the contrary definitely inhibit cissing and promote uniform drying except in very rancid samples of oil. The form in which the metal is present is also important. Resinate driers for example, always produce marked cissing and hence linoleate combinations are preferable. Cissing in pilchard oil films is also promoted by thinners such as gasoline, chlorinated hydrocarbons, estersolvents, and alcohols. It is much less common with turpentine and higher-boiling mineral oil solvents.

Figure 9c (left) shows cissing in a pilchard film containing 0.1 per cent. of manganese drier (made from fatty acids of pilchard oil). The plate on the right shows the corrective effect of adding 0.1 per cent. of lead drier. Both films were prepared simultaneously on clean black sheet-iron plates.

Whether cissing results from some kind of molecular orientation or isomerization during the initial stages of oxidation, or whether from changes in surface tension, is not known. The changes are most marked at about the end of the inductive period—long before solid film formation occurs. Undoubtedly they are closely associated with the phenomenon of wrinkle formation and the behaviour described previously with respect to films spread on mercury. The retraction of the oil spread on various solid surfaces at first suggests changes in surface tension of the oxidizing film with resulting changes in the wetting capacity. But this appears to be unlikely since the surface tension of drying films is not altered to any considerable degree up to the time cissing occurs. Moreover, the retraction of the film appears to occur, to an equal degree, on glossy and dull surfaces and regardless of the nature of the material. It is noteworthy that the surface that appears to be exposed by recession of the film is not actually exposed, but is covered by an extremely thin film which is continuous with the collected masses of oil.

Although the type of cissing seen in oil films rarely occurs in films containing pigments, the tendency nevertheless is present, and may give rise to the defect known as "pin-holing". Such films, during the initial stages of drying, become full of minute pinholes. If, when these appear the film is re-spread, they reappear within a few minutes.

Whilst the prevention of cissing in pilchard oil films may be accomplished by the proper drier combination, it is more effectively prevented by submitting the oil to a slight bodying treatment. Usually flash heating the oil to 200°C. or less followed by immediate cooling is sufficient to ensure uniform films.

BLOOMING OF FILMS

One form of bloom, namely, moisture bloom, has been mentioned in a previous section (page 20). There is still another type which, though resembling the former somewhat in appearance and often perhaps closely associated with it, is entirely different in character. This is namely the whitish greasy coating that accumulates on the surface of certain films, especially

those of fish oils or mixtures containing them. In many respects the phenomenon is analogous to the defect known as "spewing" in fat-liquored leathers. Blooming makes the film surface dull and unattractive. It is particularly troublesome because of its persistence; even after repeated removals of the bloom by rubbing the surface with a cloth dampened with a solvent, the whitish layer gradually accumulates again over a period of days or weeks.

Close examination shows that the layer of bloom consists of innumerable microscopic fatty crystals. They are highly refractile and usually show a beautiful iridescence under the polarizing microscope. They make their appearance comparatively readily on films made from, or containing, bodied fish oils; also on films baked at moderate temperatures. The crystals have a melting-point range between 46° and 90°C. If films which exhibit a tendency to bloom be immersed for some time in a solvent such as hot alcohol, a considerable quantity of the white crystalline substances can be extracted practically free from other contaminants. An analysis shows the extracted substances to be a mixture of solid fatty acids and glycerides. That this type of bloom is somewhat more pronounced with drying fish oils is not surprising in view of their relatively high content of solid glycerides. The crystalline nature of the surface bloom is shown in figures 4h and 4i taken through partly crossed nicols.

Blooming of this type, therefore, appears to be due to a squeezing-out of solid fatty acids and solid glycerides as a result of pressures within the film. It never occurs in films from unprocessed oil but it occurs extensively in polymerized and especially in baked films which undergo extensive contraction on drying. The difference in tendency to bloom between raw and polymerized oils is readily understood from the circumstance that many of the solids in the raw oil are present in the same glyceride molecules as are the drying components but on heat treatment are split off and then are free to be expelled. Oxidation during heat treatment may result in the formation of some solid mono-carboxy and di-carboxy fatty acids, products of the breakdown of unsaturated acids. Furthermore, there is evidence that during polymerization in the absence of oxygen, inter-esterification may take place with the formation of fully saturated triglycerides from mixed glycerides. This phase of the work is being investigated further. The alternate absorption and loss of moisture with the accompanying swelling and contraction are also very important factors in promoting bloom formation. This explains why the phenomenon has frequently been attributed directly to the influence of moisture.

The bloom on baked films varies in character with the temperature of baking. Oven treatment at lower temperatures usually gives rise to marked bloom which feels soft and greasy. Baking at higher temperatures tends to volatilize many of the lower melting saturated acids leaving the higher melting ones behind. When blooming occurs in such films, the surface is usually waxy and quite resistant to rubbing with the finger. If films be baked at temperatures around 300°C. all of the solids are expelled and the resulting film will no longer exhibit bloom. Such films, however, are usually too dark in colour to make high-temperature baking of any practical value except for black finishes.

In the writers' experience the only method of eliminating bloom in fish oil films is the steam distillation treatment. By removing the larger portion of solids from the oil in this way, not only is the tendency toward blooming reduced to a minimum, but the small amount of solids remaining cannot work through the dense surface layer of the film. Careful refrigeration of the raw oil at temperatures around 6°C. tends to diminish blooming of films but not to a great extent.

CONCLUSION

It is apparent from this study of film structure that the characteristic defects of pilchard and other drying fish-oil films are inherent qualities dependent upon the composition of the oils. These defects may partly be corrected by proper refrigeration of the raw oil, by selection of catalysts and by the incorporation of gums, but their complete elimination is possible only by some method which will remove the non-drying components. So far as the writers are aware, the method of polymerization and steam distillation is the only one capable of doing this satisfactorily.

SUMMARY

British Columbia pilchard oil, refrigerated at 6°C., dries more rapidly than linseed oil and yields substantial protective films. Like other drying fish-oil films, however, they are softer and more tacky than those from linseed oil. They are furthermore more permeable to moisture, become yellow in diffuse light and show a tendency to become dull and "bloom". These defects may be corrected considerably by proper choice of catalysts and by the incorporation of gums, but they can be eliminated completely only by simultaneous steam formation and polymerization of the oil at high temperatures. This treatment removes certain non-drying fatty acids which normally interfere with complete solidification of the film structure. The nature and distribution of these components are described. On removal of these, pilchard oil yields films superior to those of other drying oils in hardness, gloss, impermeability, and in freedom from yellowing and blooming.

Methods for estimating the permeability and moisture-absorbing capacity of films are described and the influence of moisture as the primary agency in film disintegration is emphasized. The nature of yellowing, cissing and blooming, and methods for correcting these defects in pilchard oil are discussed.

ACKNOWLEDGMENTS

The writers wish to express their appreciation of the assistance of Mr. P. A. Sunderland, who obtained many of the data recorded in this paper. They also acknowledge the many courtesies received from the British American Paint Co., Victoria, B.C., through their chemist, Mr. A. W. McIntyre, and from the Martin-Senour Co., Vancouver, B.C., through the manager, Mr. R. M. Ashby.

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Local Differences in the Life History of the Lobster (*Homarus americanus*) on the Coast of the Maritime Provinces of Canada

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(Received for publication September 11, 1935)

ABSTRACT

The hatching and moulting of the lobster are earlier in waters with a high than in those with a lower summer temperature. Moulting is about one week later for each degree lower summer temperature. In such high temperature areas as Malpeque bay two moultings occur during the year in most lobsters between 14 and 22 cm. in length.

In the whole southern gulf of St. Lawrence area female lobsters as small as 18 to 21 cm. in length may carry eggs, while in the Grand Manan area with a summer temperature 5 to 8°C. lower, the smallest sexually mature females are about 34 cm. in length.

The growth per moult of the female lobster falls considerably below that of the male when sexual maturity approaches, thus in the southern gulf of St. Lawrence the female growth rate slows down rapidly after 18 to 21 cm. and in southern Nova Scotia at about 30 cm.

In the southern gulf area at small sizes more males than females appear in the commercial catch, at larger sizes more females and at very large sizes nearly all the lobsters caught are males.

Average sizes of lobsters in the commercial catch are considerably smaller in the southern gulf area than in southern Nova Scotia and at Grand Manan.

INTRODUCTION

GENERAL

The lobster fishery which in recent years has been the most important fishery on the Canadian Atlantic coast must, like all fisheries for inshore animals, be subject to stringent regulations in order that the lobster population may be kept as near its maximum as possible. The regulating mechanism can only be adjusted properly when the life history of the animal is understood. Consequently a study was undertaken of the local differences in the life history of the lobster of commercial size on the coast of the Maritime provinces.

Considerable work has been done on the life history of the American lobster (*Homarus americanus*), notably by Herrick (1896, 1911) for the U.S. Bureau of Fisheries. Herrick (1896) discusses certain differences existing in time of moulting and egg-laying on various parts of the Atlantic coast of the United States, but no intensive study of differences between local populations has been made. In Canada, also, investigations on various parts of the lobster's life history have been conducted by Knight, Dawson, Huntsman, Halkett, MacKay, and others. Of these only the work of Huntsman (1923), on the relation of temperature to the success of lobster breeding, attempted to correlate differences of life history

existing on the coast with different environmental conditions. In the European species (*Homarus vulgaris*), also, there is little definite information on local differences in the life history, although Meek (1912) on the basis of measurements of lobsters made by the Board of Agriculture and Fisheries for England in 1910, says that "the minimum size of mature females varies from about 8 inches in the southern districts of England to about 9½ inches in Northumberland."

The writer is indebted to the Biological Board of Canada for bearing the expenses of work in the field, for the financial assistance afforded by three student-



FIGURE 1. Principal localities referred to in discussion of local differences.

ships and for the use of unpublished records of lobster investigations; also to Dr. A. G. Huntsman, Director of the Atlantic Biological Station, for advice during work in the field and in the preparation of this manuscript. The Department of Fisheries through the cooperation of its fishery officers made possible the collection of a large amount of data. Thanks are due to the late Dr. B. A. Bensley and the University of Toronto for providing facilities for work during the winter months; to Mr. R. V. V. Nicholls for assistance during the summer of 1931, and

to Dr. A. W. H. Needler for the cooperation of the Prince Edward Island Marine station during experimental fishing in Malpeque bay; also to Professor A. F. Chaisson of St. Francis Xavier University, under whose direction the work on average size was begun. The writer is grateful to Professor J. R. Dymond of the University of Toronto for his helpful criticism of the preliminary manuscript, and to Mr. Emile B. Paturel of Shediac, New Brunswick, for the many ways in which he aided the investigations at Pointe du Chêne,

LIFE HISTORY

Since the following paper is primarily concerned with local differences in the life history of the lobster (*Homarus americanus*), some of the accepted phases of the general life history of the animal which our observations also confirm will be taken for granted. A short outline of some of these essential preliminary features follows.

The American lobster is found only on the eastern coast of North America. There appear to be offshore movements in the fall and inshore movements in the spring so that the greater proportion of the lobsters during the warmer months of the year are congregated in a relatively narrow inshore shallow water area. Growth in length only occurs at moulting. The female after the extrusion of the eggs carries them attached to the abdomen for about eleven months before hatching.

In the following account, lobsters which at the time of examination have not moulted since the previous year will be termed old-shelled lobsters, and lobsters that have moulted since winter, new-shelled lobsters. Immediately after moulting the animal is soft-shelled; in several days it becomes paper-shelled and in a week or two rubber-shelled. A little harder condition of shell is known as buckle-shelled and in about two to six weeks, depending on size, the lobster is again a hard-shelled lobster.

LOBSTER POPULATIONS ESSENTIALLY LOCAL

Since distinct local differences in the life history of the lobster would be more likely to occur if there is little mixing between adjacent populations, a preliminary survey of the results of our tagging will be necessary. New-shelled lobsters were tagged in the Magdalen islands region, and in Malpeque bay, Prince Edward Island, during July and August, 1931. In these areas the tagging was done after commercial fishing had ceased for the year. A certain percentage of these lobsters were caught in May and June, 1932, nine to eleven months after they were liberated. Sixty-five returns were obtained from the Magdalen islands. None of the lobsters tagged in the Magdalen islands area were reported caught in any other region of the gulf. Most of the lobsters liberated were caught either at their point of liberation or within a few miles of it. The farthest distances travelled in nine to eleven months by recaptured tagged lobsters in the Magdalen islands area were only 5 or 6 miles (9 or 10 km.). Sixty-seven returns were obtained from Malpeque bay, Prince Edward Island. Of these one lobster was recaptured about 20 miles (30 km.) in a straight line and 30 miles (45 km.) following the shore line away from its point of liberation, and another about 20 miles

(30 km.) following the shore line away from where it was liberated. Eight were found outside the bay 8 to 12 miles (13 to 19 km.) east, and eight from 5 to 10 miles (8 to 16 km.) west of the point of liberation. Nine were caught near the eastern entrance to the bay, 5 to 6 miles (8 to 10 km.) from where they were liberated and the remainder were reported from various areas within the bay. The results from both areas show no definite migration but a wandering with resulting scattering, the lobster population on the whole remaining more or less local in character.

CAPTURE

Lobsters are caught in traps which have many variations but which in principle are nearly always similar to that shown in figure 2. Usually two ring entrances open into a vestibule where bait is placed, and an internal opening from the vestibule leads into the "parlour" from which few lobsters can escape.

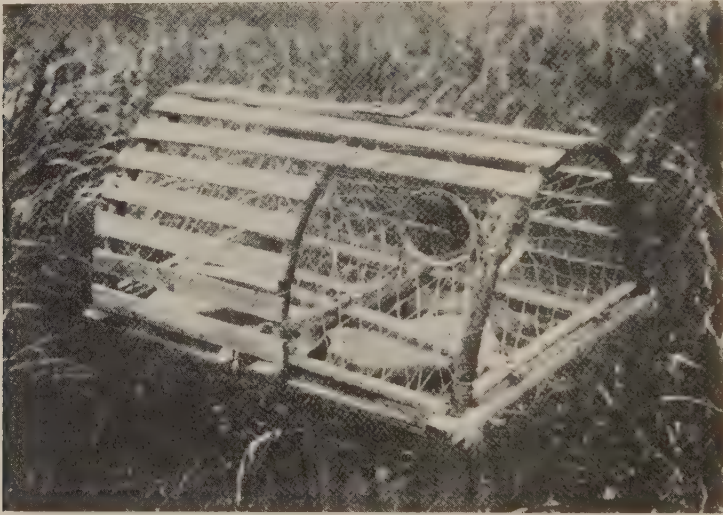


FIGURE 2.—Parlour lobster trap (after Knight 1917).

COMPARATIVE WATER TEMPERATURES IN GULF OF ST. LAWRENCE AND AT GRAND MANAN

Since certain of the warmer regions of the gulf of St. Lawrence and the area around Grand Manan will often be compared as showing extreme differences in life history, a general comparison of the temperatures in these two areas follows. Figure 3 gives a comparison of the surface temperatures at Entry island, Magdalen islands, just within the southern gulf area and at Grand Manan. These temperatures are surface temperatures taken by lighthouse keepers, but serve quite well for a comparison of conditions existing in the southern gulf and the Grand Manan areas in summer and winter. The water temperature in the gulf of St. Lawrence region (Entry island) during the summer rises about six or seven degrees centigrade higher than at Grand Manan. During the early winter the

temperature of the shallow water in the gulf falls below $0^{\circ}\text{C}.$, not rising above zero again until April, while in the Grand Manan area the temperature even at the surface rarely approaches zero. Thus the inshore water of the southern gulf region is warmer in summer and colder in winter than in the Grand Manan area.

The Entry island region is not the warmest of the southern gulf areas, but merely intermediate in nature, other areas such as Malpeque bay and the lagoons of the Magdalen islands being considerably warmer in summer.

REPRODUCTION

HATCHING

EARLIEST HATCHING

A comparison of the dates at which hatching begins in various regions has been possible by studying the reports of lobster hatcheries, which give the time of first appearance of fry in the hatchery jars. This information has been regarded as adequate to show true differences in hatching dates, since in each hatchery there would be eggs from thousands of berried lobsters obtained from the nearby fishing grounds; also the hatchery superintendents could hardly fail to note the first appearance of fry in the hatchery tanks.

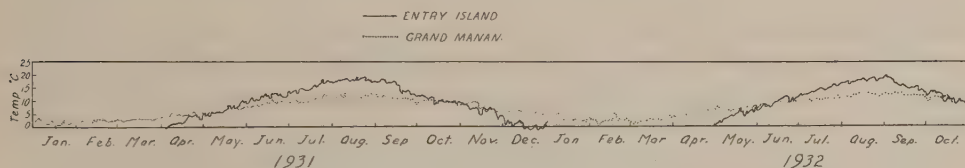


FIGURE 3. Surface temperatures at Entry island and at Grand Manan (after Hachey, unpub. MS.)

Comparison of earliest hatching in various hatcheries. Table I gives the records of first hatching in different lobster hatcheries from 1906 to 1917 arranged according to the order in which hatching apparently occurs. In the case of small differences between hatcheries, records of 1916 and 1917 do not carry as much weight as those of other years, since in these two years only the week during which the first hatching occurred is known.

There are several conditions under which differences in the time of first hatching in two hatcheries could be regarded as significant: (a) few observations in the same years with wide or constant differences in time, so that we can conclude that hatching at Buctouche is earlier than at Shemogue, and at Bay View earlier than at Inverness; (b) the differences may be smaller but the number of comparative records greater, the records from one hatchery being constantly earlier than those from the other. Thus hatching at Shemogue for the four years, when exact dates are known, occurred from 1 to 8 days earlier than at Shippigan. Hatching at Shemogue is even more definitely earlier than at Charlottetown, for although in 1912 hatching occurred in both hatcheries on the same date, in four other years the first hatching at Shemogue was from two to fifteen days earlier than at Charlottetown; (c) in some more indefinite cases a factor such as temporarily higher local water temperatures may in some years produce hatching

in one hatchery a few days earlier than in another while in most years it is considerably later. This appears to be the case at Bay View, where in 1910 hatching occurred 3 days, and in 1911, 2 days earlier than at Georgetown, while in 1912 the earliest hatching was 6 days, in 1913, 8, and in 1916, about 7 days later than at Georgetown. We conclude that normally hatching is later in the Bay View hatchery than at Georgetown.

The date of first hatching at Isaacs Harbour appears to be sometimes a little later, sometimes a little earlier than at Bay View; hatching is later at Inverness than at Bay View, while at Canso are found the latest dates of hatching in the hatcheries considered above, hatching at Canso being nearly a month later than at Buctouche.

Besides the areas shown in table I, for which observations over a number of years are available, for other hatcheries the time of earliest hatching is recorded in only one year. Various workers also have noted the earliest observed time of hatching on certain sections of the coast. These incidental observations, except for several by Mr. Andrew Halkett at Fourchu lobster pound, Cape Breton, merely give the latest possible date for the beginning of natural hatching.

In 1910 the first hatching occurred in the Magdalen islands hatchery in Pleasant bay, on June 12. In the same year hatching occurred at Shippigan, N.B., on June 14 and at Georgetown, P.E.I., on June 11. At Port Daniel hatchery in 1910 the first hatching occurred on June 26. This is the latest date of first hatching reported from any hatchery during that year, but it is not quite comparable, since owing to delay in completion of the hatchery the first eggs were not placed in the jars until June 22.

At Fourchu lobster pound, Cape Breton, in 1909, Halkett records the first hatching on July 5. In the same year the first hatching in the Canso hatchery occurred on July 2, so that Fourchu probably has a date of first hatching quite similar to that of Canso.

At Long Beach pond, St. Mary bay, 1917, the first observed hatching occurred on July 3, at the Canso hatchery in the same year, hatching began on July 12, at Isaacs harbour on June 23 and at Arichat on July 6, while in Northumberland strait the average time of beginning of hatching was June 20. In 1926 hatching was observed at Little River, St. Mary bay, on July 6.

Discussion and Conclusions

Since most of the data for a comparison of the time at which hatching begins in various regions has been obtained from the reports of lobster hatcheries giving the time of first appearance of fry in the hatchery jars, a discrepancy in the results would arise from the water in the hatchery jars being warmer than that of the sea in the neighbourhood of the hatchery. No temperatures are recorded from Canadian hatcheries, but at Woods Hole where from 1889 to 1893 the average surface temperature in the harbour was 16.7°C. for June and 20.6°C. for July, the water in the hatchery jars was found to average half a degree higher than in the harbour nearby. The bottom water in the shallow areas near the hatchery would be still lower in temperature than the surface water. The higher temperature would cause hatching in the hatchery jars to take place several days earlier

than would normally occur in nature. This, however, would chiefly affect the actual rather than the comparative dates. Moreover, since the hatcheries were situated mostly in sheltered locations (bays and harbours), the dates of earliest hatching reported from them are closely related to the absolute earliest dates of hatching in the given areas, this earliest hatching presumably taking place in the shallowest and most sheltered and consequently the warmest water.

Time in hatchery. The collection of eggs for the hatcheries usually began shortly after the lobster season opened. The Canso hatchery usually obtained its first eggs about the last of April; Shippigan, Bay View, Inverness, Charlottetown and Georgetown during the first or second week of May, and Buctouche and Shemogue about the last of May. Canso, where the eggs were placed in the hatchery jars earliest, had the latest hatching. Buctouche and Shemogue, where the eggs were placed in the jars latest, had the earliest hatching. The remaining hatcheries usually opened about the same time so that the large differences shown in table I in time of earliest hatching could not be ascribed to differences of time in the hatchery jars. It can hardly be doubted that the higher temperature in the hatchery jars would produce a faster development than in the colder sea water outside the hatchery. Thus the first hatching at Shemogue would have been even earlier and at Canso even later than that shown in table I if the eggs in the Shemogue hatchery had been placed in the jars two weeks earlier and in the Canso hatchery a week later, in this way placing all the hatcheries on the same level with regard to the time when the first eggs were placed in the hatchery jars. Since, therefore, the differences in time of first hatching shown in table I would still hold and be even increased in the cases of Shemogue and Canso if all the hatcheries had begun operations at the same time, we conclude that variations in the time during which the eggs were in the hatchery jars do not produce the differences shown.

Correlation of differences in summer bottom temperatures of shallow water areas with differences in time of first hatching in these areas. There are several ways in which a higher summer temperature could affect the time of earliest hatching: (a) in warmer waters the extrusion of eggs on old-shelled lobsters occurs earlier, and (b) the eggs once extruded would develop faster than in colder water.

The average depth in eastern Northumberland strait is considerably greater than in the western part. Consequently one would expect colder bottom water in the eastern part of the strait during summer. A few temperatures were taken in this area during the Canadian Fisheries Expedition of 1915. On June 9, in the middle of eastern Northumberland strait approximately off the Charlottetown hatchery, the temperature at 10 metres was 4.8° and at 20 metres $3.2^{\circ}\text{C}.$, while in the western part of the strait, at mid-strait off Shediack, the temperature at 10 metres was 8.1° and at 20 metres $7.0^{\circ}\text{C}.$ (Shediack is about half-way between the Buctouche and Shemogue hatcheries). On August 3, at a station off Charlottetown in the eastern strait, with a depth of 23 metres, the temperature at 20 metres was 8.4° , while in western Northumberland strait, a station at the same depth off the mouth of Egmont bay gave a temperature at 20 metres of $17.0^{\circ}\text{C}.$ In accordance with the higher bottom temperatures during the summer in the

western than in the eastern part of the strait the first hatching occurs earlier in the western area (table I).

TABLE I. Dates of first appearance of fry in lobster hatcheries along the coast of the Maritime provinces. Hatcheries arranged in order according to date of earliest hatching. The numbers used represent the number of days after May 31 that the first hatching occurred, *e.g.*, 1 = June 1

Date	Buctouche	Shenougue	Shippigan	Charlottetown	Georgetown	Bay View	Isaac's Har.	Inverness	Canso
1906			15			20			32
1907		19		27		31			40
1908		10	13	25		20			
1909		10	15	17	21				32
1910		6	14		11	8			18
1911			11		16	14	28	28	
1912		10	11	10	16	22	26	25	24
1913	7	12			19	27			26
1916	4-10	11-17	11-17	18-24	18-24	25-31	18-24	25-31	32-38
1917	10-16	17-23	17-23	17-23	17-23	17-23	17-23	24-30	36-44

Proceeding northwards toward Shippigan the nearest comparable temperature records are from the mouth of Miramichi bay at 32 metres on August 4, 1915. Here at 20 metres the temperature was 9.3° as compared with 17.0° at the same depth in western, and 8.4° in eastern Northumberland strait on August 3. Similarly in table I the first hatching of young lobsters takes place at Shippigan later than in western and about the same time as at Charlottetown in eastern Northumberland strait.

Proceeding from Charlottetown to Bay View to Inverness the channel of the strait gradually deepens from a maximum of 20 to 30 metres off Charlottetown to 50 or 55 metres off Inverness. The shores also become steeper so that the deep water approaches nearer shore. The influence of deeper cold water is to produce a lower average temperature during the summer even in the neighbouring shallow water areas, since an offshore wind causes the shifting inshore of the colder water from the deeper region. Thus temperatures of the sea near Bay View should be lower than those at the same depth at Charlottetown and those off Inverness lower than those near Bay View. Agreeing with this is a gradation in first hatching from early in Charlottetown, to later at Bay View and still later at Inverness.

The 46-metre line is about 30 miles (46 km.) offshore from Georgetown and about 5 miles (9 km.) offshore opposite Inverness. In consequence of the neighbouring shallower water the temperature of the water near Georgetown during the summer should be higher than in the neighbourhood of Inverness and in consequence hatching at Georgetown is considerably earlier than at Inverness.

Apart from being on the open coast the situation at Canso is similar to that at Inverness. In both areas there is a very narrow strip of shallow coastal water,

the depth rapidly increasing to 50 or 60 metres. Due to the lower temperatures produced by the presence of deeper colder water in the neighbourhood, Canso and Inverness hatcheries have the latest dates of hatching.

Since the differences in the dates of first hatching in hatcheries as shown in table I are produced by differences in the temperature of the sea on the lobster grounds near the hatchery, it is almost certain that differences similar to those in table I exist in the time of first natural hatching in the neighbourhood of the hatchery. The natural hatching in these areas, however, judging from the data presented in the following pages, would probably begin at least a week later than hatching in the hatcheries.

QUANTITATIVE RECORDS OF NATURAL HATCHING

Southern gulf records. In 1917 at Georgetown, P.E.I., "20 berried lobsters were placed in a pen on June 23. The pen was placed in the open sea. On July 18 only 6 were found still carrying eggs and by July 25 all 20 lobsters had shed their eggs" (MacKay, unpub. MS.).

In 1917 at Bay View near Pictou, "40 berried females were placed in an enclosure under the wharf in June. Fifteen hatched their eggs early in July. On July 30, eight of the remaining 25 still bore eggs. On 4 of these hatching was in progress and with the remaining 4 hatching apparently would not commence for at least a week" (Dawson, unpub. MS.).

Reporting on experimental fishing at Cape Traverse, P.E.I., in 1918, Dawson (unpub. MS.) says, "Hatching fry were first observed on June 21, and on July 15 out of 16 berried lobsters examined, 6 were hatching their eggs. On July 19, eleven out of 14 berried females handled were hatching and by August 1 out of 18 berried females taken by one fisherman only 4 carried old eggs." The latest record regarding old eggs was made on August 21. "On this date 2 females still carrying old eggs were taken, from one the young fry were partially hatched but the eggs on the other female appeared quite dark and it did not seem probable that in this case hatching would begin before 8 to 10 days at least."

In 1922, Dr. A. P. Knight and Mr. Andrew Halkett carried on experimental fishing in western Northumberland strait. Their method was to fish over the Prince Edward Island and the New Brunswick sides of the strait from August 1 to 15 and to cover the same ground again from August 16 to 31. At the beginning of August the percentage of berried lobsters was small on both coasts. Toward the middle of the month the percentage had increased. From August 1 to 13, 7.3 per cent of the females on the New Brunswick side were berried and 1.1 per cent on the Prince Edward Island side. By August 23 to 31 the percentage of berried lobsters had increased to 29 per cent on the New Brunswick side and 31 per cent on the Prince Edward Island side of the strait. MacKay at Shemogue, N.B., 1917, found that of two quarts of eggs (representing the eggs of about thirty berried lobsters) brought to the hatchery on July 21, half were new and half were old (unpub. MS.). Dawson, at Cape Traverse in 1918, found that on August 1 out of 18 berried females taken by one fisherman, only 4 carried old eggs (unpub. MS.). These observations from the western Northumberland strait region would seem to indicate that of the very small percentage of berried females observed by

Dr. Knight and Mr. Halkett in this area at the beginning of August, much less than half carried old eggs. Thus in 1922 in the western Northumberland strait region, hatching was practically over by August 1. Out of 14 berried lobsters recorded by Mr. Halkett from Prince county, P.E.I., on August 1 to 10, 1916, 13 had new eggs and the other had nearly completed hatching.

Out of 92 berried lobsters examined by the writer in western Northumberland strait from August 19 to September 17, 1931, only 3 obtained from the cape Tormentine deep water area (20 to 26 metres) on August 26 carried old eggs. From each of these 3, all except a few of the eggs had hatched, there being 5 or 6 probably spoilt eggs remaining on 2 of the lobsters, and 40 or 50 healthy eggs on the other.

In 1932, during experimental fishing by the writer at Medea rock, Shediac bay, in western Northumberland strait from June 27 to July 20, the first berried lobster with eggs hatching was taken on July 9. Among 15 berried lobsters taken between July 1 and 14, 4 had eggs hatched or hatching, while among 15 berried lobsters taken between July 17 and 20, 11 had eggs hatched or hatching. Out of 85 berried lobsters examined by the writer at Pointe du Chêne from August 24 to September 14, only 1 caught on August 24 in the middle of the strait at a depth of 16 metres carried old eggs, and even on this lobster there were only 5 or 6 eggs which were possibly dead. Of 26 berried lobsters examined at Summerside on September 19, none carried old eggs, while among 12 berried lobsters examined at cape Tormentine on September 21-22, 1 female caught off Victoria harbour in eastern Northumberland strait in 20 to 29 metres carried its full complement of old eggs, which were ripe and would have begun hatching within several days.

Malpeque bay, P.E.I. In a total catch of about 1,500 lobsters caught in Malpeque bay from July 24 to August 13, 1931, 9 berried lobsters were captured, all of which carried new eggs.

Magdalen islands. Halkett (1920) records that at Havre Aubert, Amherst island, on July 2, 1919, 2 berried lobsters examined had both completed hatching, and at Entry island on July 14 out of 10 berried lobsters, 2 had nearly finished hatching, 4 were hatching, on 2 the eggs were ripe, and on the remaining 2 were not ripe.

During experimental fishing by the writer, $\frac{1}{4}$ mile (0.4 km.) off Grindstone cape in Pleasant bay, from July 7 to 14, 1931, out of 8 berried lobsters captured, 1 had nearly completed hatching, 1 had eggs ready to hatch and the remaining 6 possessed old eggs not yet fully developed. From July 20 to July 31, 6 berried lobsters were obtained, 2 of which possessed new eggs, 3 had nearly completed hatching, while on 1 caught on July 20 the eggs were not ripe.

Of 6 berried lobsters caught in House Harbour lagoon from July 11 to 27, 1931, from 3 the eggs had completely hatched while the other 3 had nearly completed hatching, only a few eggs remaining.

Discussion and Conclusions

From the records of Dawson at cape Traverse in 1918 and of the writer during experimental fishing in Pleasant bay, Magdalen islands, 1931, and in

Shediac bay, western Northumberland strait in 1932, it would seem that in these areas only a very small amount of hatching occurs in June.

The effect of higher summer temperature in hastening the time of completion of hatching is apparent throughout the records. Hatching in House Harbour lagoon, Magdalen islands, is completed much earlier than in the neighbouring colder water of Pleasant bay. In Malpeque bay, where, also, from comparable records, the temperature of the water on the fishing ground in 1931 was at least as high as in House Harbour lagoon, hatching is completed early in July.

In western Northumberland strait, hatching is nearly over by the first of August, and it is certainly completed by August 20, except in the deep cold water between cape Tormentine, N.B., and cape Traverse, P.E.I., where in some years at least an occasional lobster may not have completed hatching by September 1. In the still colder deep water of eastern Northumberland strait hatching may not be completed before the end of September.

EGG-BEARING LOBSTERS

SMALLEST SIZES OF MATURE FEMALES

Figure 4 and table II show the smallest sizes of berried lobsters found at various points on the coast of the Maritime provinces.

Since fishermen are required by law to return to the sea all "berried" (egg-bearing) lobsters, the determination of the size at which females begin to bear eggs, from the examination of commercial catches, is attended with some difficulty. It has been our experience, however, that fishermen often overlook the berried condition of small females and it has thus been possible to find considerable numbers of small berried females in the commercial catches. The data included in table II were obtained from the examination of such catches except in the case of Pointe de Chêne, Summerside, Sea Cow head, North lake, Crown point, Shemogue and Grand Manan, where fishermen sometimes brought whole catches ashore for examination, and at Grindstone, Magdalen islands, where the berried lobsters were caught during special fishing.

In areas for which we obtained no berried lobster measurements, other measurements, mostly by Mr. Andrew Halkett and Professor MacClement, have been used.

Regional differences. In figure 4 no wide differences in the size of the smallest egg-bearing lobsters recorded are apparent in the gulf region from Chaleur bay to the strait of Canso in eastern Nova Scotia, this region including Prince Edward Island and the Magdalen islands. Small sizes of egg-bearing lobsters similar to the gulf sizes are also found in eastern cape Breton and along the coast of Nova Scotia at least as far south as Liscomb. In all these areas lobsters between 18 and 21 cm. in length were found carrying eggs. South of Liscomb the scanty records indicate a gradual rise in the smallest size at first maturity from Port Dufferin towards southwestern Nova Scotia with a still further rise at Grand Manan, where the smallest lobster found carrying eggs was 34.6 cm. in length. (The region between Port Dufferin and Lockeport has not been covered by the writer, and from other than scientific sources it seems probable that in St. Mar-

garets and Mahone bays at least, lobsters as small as in the gulf area may be found carrying eggs.) The indicated sizes at first egg-bearing in the bay of Fundy are somewhat similar to those at Grand Manan, with the possibility of a slightly smaller size at first egg-bearing toward the head of the bay, from which area no records by scientific workers are available. A berried lobster of 27.9 cm. was reported from St. Mary bay by MacClement in 1917 (unpub. MS.).



FIGURE 4. Smallest sizes of egg-bearing lobsters found during lobster measurements (centimetres).

Illustrating also the differences between the essentially gulf and the southern Nova Scotia regions in size of the female at maturity are various quantitative records. In Dawson's (unpub. MS.) measurements at cape Traverse, P.E.I., in 1918, of 374 unselected berried lobsters, 25.9 per cent were 22.9 cm. or under, and 63.4 per cent 25.4 cm. or under. At the lobster pound at Fourchu in eastern Cape Breton, 1909, out of 2,929 unselected berried lobsters collected from neighbouring areas and measured by Mr. Halkett, 9.1 per cent were below 22.9 cm. and 48.5 per cent under 25.4 cm. In 1917, according to MacClement (unpub. MS.), 1,000 male and 1,000 female lobsters, all over 25.4 cm. in length, were

TABLE II. Length in centimetres of the smallest egg-bearing lobster found in lobster measurements on different parts of the coast of the Maritime provinces

Date	Locality	Size of smallest berried lobster measured	No. of berried lobsters measured	Total no. of lobsters measured
June 10, 1930	Stonehaven, N.B.....	20.0		187
June 19, 1930	Burnt Church, N.B.....	19.0		1003
June 27, 1932	Richibucto cape, N.B.....	18.5	6	
Sept. 2, 1932	Pte. du Chêne, N.B.....	18.0	139	10005
Aug. 24, 1931	Off Shemogue head, N.B.....	19.5	27	558
Sept. 22, 1932	Cape Tormentine, N.B.....	20.8	12	1886
June 23, 1931	Pugwash, N.S.....	20.0	2	1225
June 24, 1931	Malagash, N.S.....	21.3	9	1744
June 26, 1931	Cariboo, N.S.....	19.6	7	2893
June 19, 1931	Belle river, P.E.I.....	22.0	7	1271
June 20, 1931	Crown point, P.E.I.....	22.5	23	264
Sept. 22, 1932	Canoe cove, P.E.I.....	20.3	10	
Sept. 5, 1931	Off Sea Cow head, P.E.I.....	19.2	26	1378
Sept. 9, 1931	Summerside, P.E.I.....	19.5	36	1696
Sept. 12, 1931	West point, P.E.I.....	18.5	1	731
June 5, 1931	Campbellton, P.E.I.....	19.8	6	1045
June 4, 1931	Miminigash, P.E.I.....	20.0	10	923
June 8, 1931	Skinner's pond, P.E.I.....	19.0	1	382
June 10, 1931	Malpeque bay, P.E.I.....	20.2	5	567
June 10, 1931	Darnley basin, P.E.I.....	20.2	2	1287
June 16, 1931	North lake, P.E.I.....	21.0	19	1959
July 5, 1930	Cape Dauphin, N.S.....	18.5		933
June 10, 1932	Canso, N.S.....	20.4	1	111
June 11, 1932	Charles cove, N.S.....	20.4	1	841
June 13, 1932	Liscomb, N.S.....	19.8	1	963
June 15, 1932	Port Dufferin, N.S.....	22.2	10	1156
July 20, 1931	Grindstone, Magdalen Is.....	19.8	16	730
May 23, 1931	Port Latour, N.S.....	29.0	1	1079
May 23, 1931	Seal Island, N.S.....	32.0	2	2938
May 27, 1931	Ledge harbour, N.S.....	29.0	2	979
June 3, 1932	Seal cove, Grand Manan, N.B.....	34.6	9	
May 25, 1932	Seeley's basin, N.B.....	36.5	2	79
(Measured by A. Halkett)				
June 13, 1923	Lismore, N.S.....	21.0	3	
June 18, 1923	Ballantyne's cove, N.S.....	19.1	8	
June 23, 1923	Harbour au Bouche, N.S.....	20.3	18	
July 11, 1923	Gabarus, N.S.....	20.3	4	
June 15, 1916	Musquodoboit, N.S.....	24.6	1	
May 17,	Port Mouton, N.S.....	25.4	3	
(Measured by W. T. MacClement)				
Sept. 3, 1917	Long Beach pond			
	St. Mary bay, N.S.....	27.9	4	
1917	Little River St. Mary			
	bay, and Whale cove.....			
	Tommy's beach and White cove, bay of			
	Fundy.....	31.8	40	
(lobsters kept in lobster pd.)				
(Measured by C. Rafuse)				
1932	Advocate harbour, bay of Fundy.....	29.0	21	

placed in Long Beach pond, a lobster pound in St. Mary bay, N.S. Half the lobsters came from St. Mary bay, and half from the bay of Fundy nearby. Three-quarters of the lobsters were under 30.5 cm. in length. Forty lobsters extruded eggs in the pond and all these lobsters were over 31.5 cm. in length. In Whitehead and Woodward's cove pounds, Grand Manan, 1932, were male and female lobsters measuring 23 cm. and over, obtained in the region from cape Sable in southwest Nova Scotia to Grand Manan, a large proportion of the lobsters over 25 cm. in length being from Grand Manan. Of 31 berried lobsters obtained from these pounds by the writer in August 1932, the smallest was 27.9 cm. long. The remainder were all over 30 cm., only 3 being below 34 cm. in length.

Local differences. These are in general smaller than the regional differences and in most cases the local differences shown in figure 4 are to be regarded only as indications, since these small differences require a great number of records before we can depend very much on the results.

In Prince Edward Island the smallest sizes of berried lobsters so far recorded are in the western part of the island. On the north-east and south-east coasts of the island the indicated sizes are from 1 to 3 cm. larger than in the western part. In western Northumberland strait the indicated sizes at first maturity are on the whole smaller than in the eastern part of the strait. In St. Mary bay smaller berried lobsters are recorded than at Grand Manan at the mouth of the bay of Fundy.

RELATIVE NUMBERS OF BERRIED LOBSTERS

In table III the relative number of females carrying eggs is expressed as a percentage of the total number of lobsters (including berried lobsters) in the corresponding catch. As far as could be determined all the catches are whole catches including all the berried lobsters caught. Most of the entire catches were obtained from fishermen who on request brought entire catches ashore, and in these cases the percentage of berried lobsters shown in table III is the minimum, since there remains the possibility that these fishermen may have thrown an occasional berried lobster away. The number of berried lobsters, however, caught at Grand Manan is the exact number in the catch. The results obtained from the experimental fishing offers a useful check on the catches obtained from the fishermen.

Small variations in the percentage of berried lobsters in the catch at different dates might be due to the returning of berried lobsters to the sea as compelled by law while non-berried lobsters were retained, or to differences in the enforcement of this law in various areas. Again variations in the percentage of berried lobsters obtained during the spring and the fall seasons might be due to differences existing in the shell condition of the lobster at these times. Differences in the number of small lobsters below mature size in the catch from different areas would also affect the berried lobster abundance expressed as a percentage of the whole catch. For these reasons it would be unwise to attempt distinctions between the various gulf areas on the basis of the results in table III. However, it is evident that the percentage of berried lobsters present in all the southern gulf areas is immensely greater (from 6 to 20 times in the figures of table III) than

at Grand Manan, and this in spite of the fact that no lobsters smaller than 19 cm. are included in the total catch at Grand Manan, while in nearly all the gulf regions a large percentage of the catch is below this size. If as many small lobsters were included in the Grand Manan calculations as in those of the gulf regions the percentage of berried lobsters at Grand Manan would be still smaller than the 0.4 per cent shown in table III.

TABLE III. Percentage of berried females in the entire lobster catch in various areas

Date	Locality	Total no. of lobsters in catch	Total berried females in catch	Percentage berried females in catch
1931				
July 7-Aug. 5	Magdalen Islands—Grindstone*.....	388	14	3.6
June 16	North-East P.E.I.—North Lake.....	1026	ca. 24	ca. 2.3
June 20	South-East P.E.I.—Crown Point.....	287	23	8.0
Aug. 24	Western Northumberland strait off Shemogue head, N.B.....	585	27	4.6
Sept. 9	Summerside, P.E.I.....	201	15	7.5
1932				
Sept. 19	" ".....	299	20	6.7
June 27-July 20	Pointe du Chêne*.....	614	32	5.2
Aug. 31-Sept. 14	" " ".....	732	57	7.8
May 31-June 2	Grand Manan—Seal Cove.....	1028	4	0.4
Aug. 3-Aug. 18	" " " *.....	365	0	0.0

*Experimental fishing.

Discussion and Conclusions. On the whole the size of the female at first sexual maturity is smallest (18 to 21 cm.) in the southern gulf of St. Lawrence region from bay Chaleur to the strait of Canso and southwards along the eastern Nova Scotia shore as far as Liscomb. The size at first sexual maturity is largest (about 28 to 35 cm.) in southern Nova Scotia west of cape Sable island and in the bay of Fundy. The southern part of the gulf of St. Lawrence and the Grand Manan fishing area are probably the extremes and in both of these areas the sizes of the smallest mature females shown in figure 4 are fairly well substantiated. Even more striking is the contrast between the southern gulf and the Grand Manan regions if we consider age and weight. Our present knowledge of the growth rate of the lobster indicates that in the Pointe du Chêne region in western Northumberland strait the smallest mature female would be 3 or 4 years old while the smallest mature female at Grand Manan would be at least 9 years old. The smallest sexually mature females at Pointe du Chêne weigh about 7 ounces (22 gm.), while the smallest mature female at Grand Manan weighs about 44 ounces (137 gm.). Table IX gives a comparison of summer temperatures on the lobster fishing grounds in typical gulf areas and at Grand Manan. The Grand Manan areas during the summer are seen to be much lower in temperature than the gulf areas compared, and it is certain that the inshore areas around the whole gulf from bay Chaleur southwards have a summer temperature considerably

higher than similar inshore areas at Grand Manan. Thus high inshore summer temperatures are correlated with early maturity and low inshore summer temperatures with a late maturity.

The temperature of western Northumberland strait is on the whole higher than that of eastern Northumberland strait and the differences shown in figure 4 between these two areas especially in the case of the apparent larger size at first maturity in southeastern Prince Edward Island is possibly due to this temperature difference, but the difference in smallest mature sizes is probably not so great as appears in figure 4, since the western part of the strait has been investigated much more thoroughly, and consequently there would be a greater chance of finding smaller berried lobsters. The water at the head of St. Mary bay is definitely warmer during the summer than at Grand Manan. Agreeing with this the size at first maturity is smaller in St. Mary bay than at Grand Manan.

Our theory to account for the above differences is that the size at which the female becomes sexually mature is the result of differential growth of the ovary and the remainder of the body. The development of all parts of the body would be either at a standstill or at a very low ebb during the period of low temperature in the winter months. The much faster development in the high summer temperatures would so far outweigh the slow winter development that differences in winter temperature cannot be correlated either with growth of the body as a whole or with the development of the ovary. The higher summer temperatures in the gulf are favourable for the growth in length of the lobster but even more favourable for ovarian development, so that the animal becomes mature at a small size and an early age. The lower summer temperatures at Grand Manan are still suitable for digestion and for general body growth but apparently very unfavourable for ovarian development, so that the animal grows to a large size before becoming sexually mature.

The much smaller percentage of the lobster population carrying eggs at Grand Manan than in the gulf of St. Lawrence areas is directly due to the large size at which maturity begins at Grand Manan. With intensive trapping very few females in this area can reach the large size at which sexual maturity begins. The small percentage of the population, 0.4 per cent found carrying eggs at Grand Manan, is really greater than that under natural conditions, since many berried lobsters which have extruded eggs in the lobster pounds at Grand Manan are liberated each year, and this artificially adds to the percentage of egg-bearing lobsters in the fisherman's catches.

GROWTH

MOULTING IN LOBSTERS OF COMMERCIAL SIZE

The data used for a general consideration of local differences in the rate of moulting were obtained from experimental lobster fishing in House Harbour lagoon and in Pleasant bay, Magdalen islands, and in Malpeque bay, Prince Edward Island, 1931, and at Pointe du Chêne and Grand Manan, 1932, together with an examination of the shell condition in 11,562 lobsters in western Northumberland strait during the fall season of 1931, and in 4,718 lobsters from the same area in 1932.

The shell condition of the lobster varies with the time that has elapsed since it has moulted. Immediately after moulting the shell is very soft, gradually hardening until in a few weeks the lobster reaches a hard-shelled condition.

In the tables given, certain symbols have been used to denote shell condition.

"O" equals old shell; the lobster has not moulted since the previous year at least.

"m" equals the shell condition of an old-shelled lobster, preparing for moulting. Lobsters are distinguished as preparing for moulting by the dull colours of the shell, the deep reddish tint of the membranes at the joints and in cases far advanced, by absorption areas in the shell.

"P" equals paper shell, the shell being about as stiff as parchment.

"R" equals rubber shell. When the lobster possesses an elastic and rubber-like condition of shell it is known as rubber-shelled.

"B" equals buckle shell. When the carapace has hardened beyond the rubber-shelled stage but can still be easily buckled between thumb and finger, the lobster is described as buckle-shelled.

"N" equals new hard shell. The lobster has moulted since the previous winter and has become hard-shelled again. The shell, however, is not as thick as that of the old-shelled lobster.

"M" equals the shell condition of a new-shelled lobster preparing for moulting; that is, a lobster which has already moulted once in the early summer and is preparing for a second moult.

TIME OF FIRST MOULTING OF THE YEAR

1931

Magdalen islands. Table IV shows the shell condition of lobsters caught in Pleasant bay, Magdalen islands, from July 7 to August 5, 1931. Only 9.8 per cent of the lobsters captured from July 7 to July 10 were new-shelled. By July

TABLE IV. Lobster catches from Meule Rock, $\frac{1}{4}$ mi. (0.6 km.) off Cape Meule 8 metres deep, and near Cape Meule wharf 40 yds. (40 m.) from shore 3 metres deep, during experimental fishing in Pleasant bay, Magdalen islands, 1931. O,—old shell; m,—old shell moulting; P,—paper shell; R,—rubber shell; B,—buckle shell; N,—new hard shell.

Date	Old-shelled O m	New-shelled P R B N	Total lobsters	Percentage new-shelled
1931				
July 7	3 1		4	0
July 8	10 2	1 1 1	15	20.0
July 9	8 0	1	9	11.1
July 10	12 1		13	0
July 14	17	1 2 3	23	26.1
July 15	6 1	1 3 1	12	41.7
July 20	27 5	2 2 7 5	48	33.3
July 24	23 2	3 3 14 6	51	51.0
July 25	6 1	1 15 13	36	80.6
July 28	7 3	2 22 11	45	77.8
July 31	4 1	2 1 34 24	66	92.4
Aug. 5	2	1 2 20 41	66	97.0

20 new-shelled lobsters constituted about one-third of the catch, by July 31, 92.4 per cent, and on August 5, 97.0 per cent of the lobsters caught were new-shelled.

When fishing in House Harbour lagoon, Magdalen islands, was begun on July 10, all except a few lobsters were new-shelled, the majority being hard-shelled. Between July 10 and July 15, 126 lobsters were caught, of which 94.4 per cent were new-shelled, 60.3 per cent being hard-shelled. Not a single lobster preparing for moulting was observed during the capture of over 1,500 lobsters from July 10 to August 10. Thus by July 10 to 15 the lagoon lobsters had reached a stage of shell condition not attained by the Pleasant bay lobsters until some

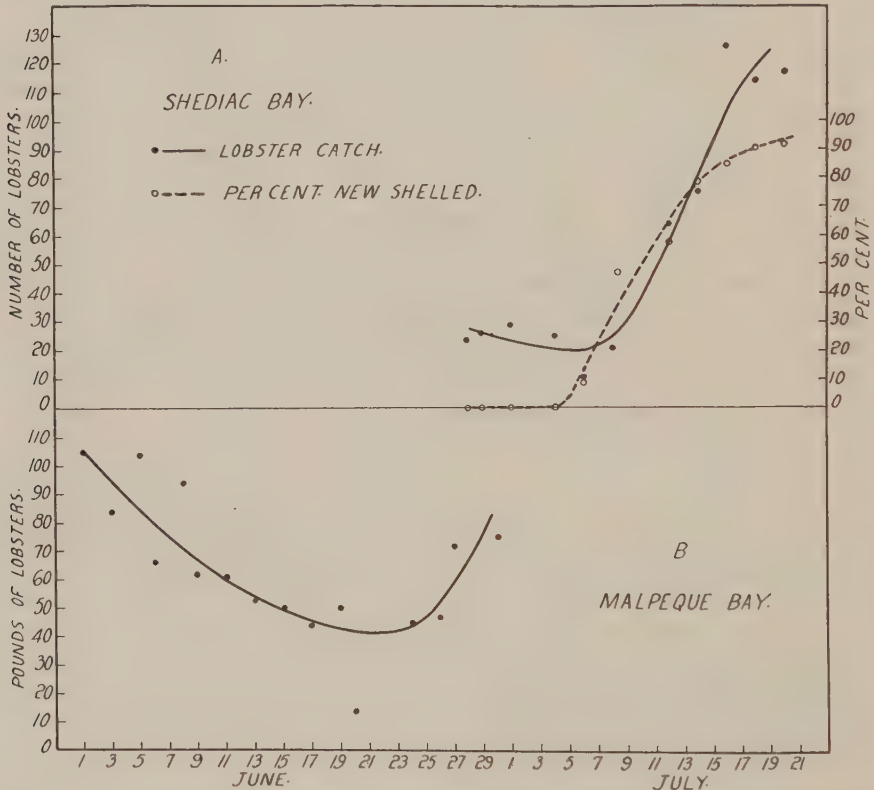


FIGURE 5. A,—Correlation of increase in the number of lobsters caught in 47 traps during experimental fishing at Pte. du Chêne, 1932, with increase in the percentage of new-shelled lobsters in the catch. B,—Total lobster catch of a fisherman, fishing on Hog island reef, Malpeque bay 1931, during the last month of the fishing season ending on June 30.

time between July 31 and August 5, this being the time at which practically all moulting was over on the Pleasant bay fishing ground. Thus moulting in the lagoon must have started not much later than the middle of June, the height of the moulting period probably being during the last week of June and perhaps the first few days of July. A difference of about three weeks is therefore evident in the general moulting period on the lagoon and Pleasant bay fishing grounds which were only about 3 miles (5 km.) apart.

Malpeque bay. According to Dr. A. W. H. Needler, Mr. F. England, a Malpeque bay fisherman says of the 1931 season that there was very poor fishing in Malpeque bay during the middle of June, indicating that the lobsters were preparing for moulting and not trapping well. During the last few days of June, many lobsters were new-shelled and the usual increase in catch with the new shell condition took place. Lobsters do not eat much and are not very active immediately before moulting and thus are not readily trapped at that time. For several days after moulting the food mostly consists of pieces of shell. Under the influence of this diet the shell of the lobster hardens and in a few days after moulting the lobsters which are ravenously hungry are readily caught in traps. Figure 5A shows the correlation of the increase in the total catch of lobsters (using the same number of traps on the same fishing ground) obtained at Pointe du Chêne in 1932, with the number of new-shelled lobsters present. It will be noted that after a period with a small catch in the old-shelled condition, the number of lobsters caught per day gradually increases as the percentage of new-shelled lobsters in the catch increases. Figure 5B, representing the catch per day's fishing of a fisherman on Hog island reef, Malpeque bay, 1931, shows a sharp rise in the catch occurring about June 25 to 30, indicating that from this time onward the new-shelled lobsters were forming an increasing part of the catch. The above is substantiated by the results of the experimental fishing on Hog island reef, Malpeque bay, carried on by R. V. V. Nicholls from July 24 to August 14, 1931. When fishing was begun on July 24 the lobsters were nearly all new and hard-shelled.

1932

Shediac bay. Table V gives the shell condition of the lobsters caught during experimental fishing in Shediac bay, western Northumberland strait, from June 27 to July 20, 1932. No new-shelled lobsters were caught before July 6 but the

TABLE V. Lobster catches from Medea rock, Shediac bay 4 to 5 fathoms ($7\frac{1}{2}$ -9 metres) deep during experimental fishing at Pointe du Chêne, N.B., 1932. O,—old shell; m,—old shell moulting; P,—paper shell; R,—rubber shell; B,—buckle shell; N,—new hard shell

Date	No. of traps	Old shell O m	New shell P R B N				Total lobsters	Per cent. new-shelled
1932								
June 27 & 28	24	10 2					12	0
June 29	24	9 4					13	0
July 1	35	16 6					22	0
July 4	35	13 6					19	0
July 6	47	8 2	0	0	1		11	9.1
July 8	47	10 1	0	1	9		21	47.6
July 12	47	20 7	1	3	26	7	64	57.8
July 14	47	12 4	1	2	21	35	75	78.7
July 16	47	14 5	0	6	50	51	126	84.9
July 18	47	7 4	0	2	31	70	114	90.4
July 20	47	9 1	0	5	47	55	117	91.5

N.B.—Berried lobsters are not included in the above figures, but females which have recently hatched their eggs are included.

proportion of recently moulted lobsters in the catch rapidly increased after July 6, until by July 20, 91.5 per cent of the lobsters caught had recently moulted. Thus by July 20 in Shediak bay, 1932, approximately the same percentage of the population had moulted as by July 31, 1931, on the Pleasant bay, Magdalen islands fishing ground (see table IV).

Grand Manan. In special fishing on the inshore fishing grounds mostly 200-300 yards from shore in 2-4 fathoms (4-8 m.) at Seal cove, Grand Manan, from August 3 to 17, 1932, 365 lobsters were caught. Only two of these, one obtained on August 15 and the other on August 17, were new-shelled. The remaining lobsters were all old-shelled as determined by hardness of shell, scratches on the shell, and the claws on boiling being packed tightly with meat. Owing to the late date at which moulting begins in this region, and from fishermen's accounts of the softness of shell of lobsters when the Grand Manan season opens on November 15, it is probable that in this area the greater part of the moulting is in September.

Malpeque bay. From information obtained from Dr. Needler and others it would appear that a rise in the catch of lobsters in Malpeque bay, P.E.I., owing to more lobsters being caught in the new-shelled condition, occurred in 1932 before the end of June and that this is a usual occurrence in Malpeque bay.

NUMBER OF MOULTINGS

The approach of a moulting period among lobsters may be noted first by the appearance in the catch of lobsters preparing for moulting, new-shelled lobsters with very thin shells appearing a few days later. To reach what is known as the hard-shelled condition, in western Northumberland strait the small new-shelled lobsters (below 23 cm.) require several weeks and the larger lobsters a longer time, increasing with size. For several weeks before moulting a lobster may be identified as preparing for moulting by various characteristics already noted. Lobsters in this state, however, are sluggish and do not trap well, consequently even immediately preceding the maximum moulting only a relatively small percentage of these lobsters preparing for moulting appear in the catches.

Two moultings among the smaller lobsters in western Northumberland strait

1931. During the fall season of 1931, in the Pointe du Chêne and Summer-side areas of western Northumberland strait, from August 19 to 24 (table VII), nearly all the small lobsters (below 23 cm.) showed by their new shells that they had already moulted once since winter, and few small lobsters were preparing to moult or had moulted recently, nearly all the small lobsters being new-shelled and hard. From August 27 to September 9 in these areas a large number of the small lobsters were moulting and a still greater number showed by the soft condition of their shells that they had recently moulted. In 1931, at Pointe du Chêne, only 1.7 per cent of the lobsters in the catch were recorded as preparing for moulting on August 19 and 20, the percentage rising August 27 to September 3 to 6.1 per cent, and had so decreased by September 16 to 18 that at this time only 0.6 per cent of the catch were preparing for moulting (see table VI).

1932. During experimental fishing at Pointe du Chêne from June 27 to

TABLE VI. Percentage of the lobster catch at Pointe du Chêne (mostly from Medea rock, Shediac bay) preparing for moulting at various periods in 1931 and 1932

Date	Locality	Per cent. of total catch preparing for moulting	Total lobsters	Remarks
1932				
June 27-July 4	Medea rock, Shediac bay.....	27.3	66	Special fishing
July 6-12	" " " "	10.4	96	"
July 14-16	" " " "	4.5	201	"
July 18-20	" " " "	2.2	231	"
Aug. 24-31	Pte. du Chêne, N.B.....	9.7	2259	
Sept. 12-14	Catches mostly from Medea rock....	3.3	1047	
Sept. 28-29	Catches mostly from Medea rock....	0.6	469	
1931				
Aug. 19-20	Pte. du Chêne, N.B. catches	1.7	1816	
Aug. 27-Sept. 3	Mostly from Medea rock.....	6.1	1736	
Sept. 16-18	" " " "	0.6	1222	

July 20, 1932, no new-shelled lobsters were caught before July 6. From July 6 onward new-shelled lobsters appeared in the catch, the percentage gradually increasing until by July 20 when fishing ceased, 91.5 per cent of the catch consisted of new-shelled lobsters that had recently moulted. The remaining 8.5 per cent were old-shelled, showing by their hard shells, dull, scratched and dirty, that they had not moulted since the previous year (see table V). By analogy with the catches obtained in Pleasant bay, Magdalen islands, during July and August, 1931 (table IV), the moulting period on the Pointe du Chêne fishing ground in Shediac bay would in 1932 have been over (except for a few stragglers) before the end of July. When the lobster fishing season began in western Northumberland strait, lobsters were again examined at Pointe du Chêne. Out of 2,259 lobsters examined from August 24 to 31, 1932, all except 0.2 per cent of the lobsters below 23 cm. in length and 8.5 per cent of 23 cm. and over in the catch had moulted since winter. Many of the small lobsters below 23 cm. were again preparing for moulting or had recently moulted and were soft-shelled. Practically all the small lobsters preparing for moulting showed by their relatively clean and thin shells that they had previously moulted during the early summer. Table VI shows the percentage of the lobster catch at Pointe du Chêne preparing for moulting during the experimental fishing in June and July, 1932, and during the commercial fishery later. From July 27 to July 4, 27.3 per cent of the total catch was preparing for moulting, with a gradual decrease in the percentage until from July 18 to 20 only 2.2 per cent of the lobsters caught were getting ready for moulting. All these lobsters were preparing for moulting for the first time since winter. When lobsters were again examined from August 24 to 31, the percentage of lobsters preparing for moulting had risen to 9.7 per cent, with another gradual decrease until from September 28 and 29 only 0.6 per cent of the lobsters were preparing for moulting. (The August and September percentages

TABLE VIII. Percentage of old-shelled lobsters in total catch, and the percentage of new-shelled lobsters in various conditions of shell in the Pte. du Chêne and Summerside areas August 27 to Sept. 9, 1931. *Fishing grounds:* August 27-Sept. 3, Pte. du Chêne inshore, 6-9 metres, 1,736 lobsters; August 27-Sept. 3, Pte. du Chêne offshore, 7-18 metres, 1,037 lobsters; Sept. 5, Summerside inshore, 6-7 metres, 142 lobsters; Sept. 5-9, Summerside offshore, 11-18 metres, 805 lobsters.

Size cm.	Male						Female						Total	
	O	N	M	B	R	P	O	N	M	B	R	P	Male	Females
12														2
13													5	2
14									89.5	10.5			9	19
15		77.4	9.5	8.2	4.8			83.0	8.5	8.5			84	47
16		68.0	13.7	19.0	0.7	0.7		77.7	11.6	9.8	0.9		153	112
17	0.4	53.4	13.6	28.0	4.2	0.8	0.6	64.4	10.7	20.9	3.4	0.6	237	178
18	0.4	46.5	10.0	36.1	7.1	0.4		57.2	11.6	25.6	4.2	1.4	270	215
19	0.3	37.1	8.5	41.4	12.7	0.3		45.5	5.2	40.8	7.3	1.0	308	191
20	0.3	29.8	5.2	47.2	15.7	2.0	0.6	38.5	4.3	46.0	9.9	1.2	306	162
21	0	18.7	5.3	40.8	32.8	2.3	0.9	38.5	5.5	39.4	16.5		262	110
22	0.4	23.6	2.8	42.7	30.1	0.8		24.7	3.7	48.1	21.0	2.5	247	81
23	1.1	18.4	2.8	47.5	30.7	0.6		31.0		44.8	24.1		181	29
24	1.8	30.7	5.6	31.5	30.6	1.9		27.3		57.6	15.2		110	33
25	2.4	35.8	1.2	34.6	27.2	1.2		39.3		46.4	14.3		83	28
26	17.1	50.0		32.4	17.6		2.6	48.6		45.9	5.4		41	38
27	3.2	60.0		30.0	10.0			36.7		50.0	13.3		31	30
28	23.5	69.2		23.1	7.7			25.8		64.5	9.7		17	31
29	30.8	100.0						20.0		64.0	16.0		13	25
30													4	6
31													3	7
32													2	3
33													0	2
34													1	1
35														0
36														1
30-32	22.2	100.0						18.8		50.0	31.3			
													2367	1353

possibly the very largest sizes caught. Any significant decrease in the percentage of hard-shelled specimens among the new-shelled lobsters in this area after August 19 to 24, especially among the smaller lobsters, must therefore be due to the second moulting already referred to.

Figure 6 compares the percentage of male and figure 7 the percentage of female new-shelled lobsters of various sizes with hard shells in the Pointe du Chêne and Summerside area from August 19 to 24, with the percentage of new-shelled lobsters with hard shells from the same area from August 27 to September 9. If there were no further moulting after August 19 to 24 in the Pointe du Chêne and Summerside area, the percentage of the new-shelled lobsters possessing hard shells would increase at all sizes owing to the gradual hardening of the shell in buckle- and rubber-shelled lobsters.

Second moulting of males, 1931 (Figure 6, tables VII and VIII). In the Pointe du Chêne and Summerside area, 1931, on August 19 to 24 the percentage of hard-shelled specimens among the new-shelled lobsters gradually decreased from 100 per cent at 14 cm. to 32 per cent at 31 cm. Observations of shell condition during the period August 27 to September 9 in the same area showed at all sizes below 27 cm. a decrease in the percentage of new-shelled lobsters with hard shells, an effect which as shown above could only have been produced by a second moulting during 1931.

The greatest effect of this second moult was observed at sizes 21 to 23 cm., for example, at 23 cm. the percentage of the new-shelled male lobsters with hard

shells declined from 75.3 per cent on August 19 to 24, to 18.4 per cent during the period August 27 to September 9. During the latter period at sizes below 21 cm. and above 23 cm. there was an increase in the percentage of hard-shelled specimens among the new-shelled lobsters in the catch. Since small lobsters presumably moult oftener and regain the hard-shelled condition more quickly than larger lobsters, the gradually increasing percentage of hard-shelled lobsters at progressively smaller sizes is to be attributed to a quicker hardening of the shell in these sizes after the second moult.

Among the larger males enough time has elapsed since August 19 to 24 for the new-shelled 29 to 32 cm. males to become 100 per cent hard-shelled by the

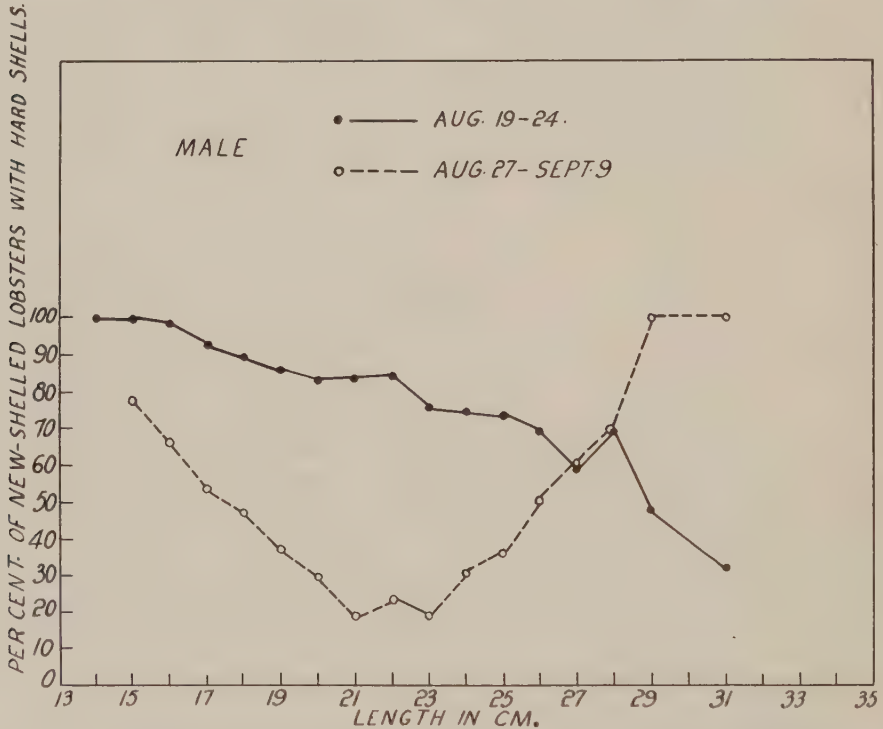


FIGURE 6. Percentage of new-shelled male lobsters of different sizes with hard shells in catches of 4555 lobsters in the Pte. du Chêne and Summerside area from August 19-24 and of 3720 lobsters in the same area from August 27-September 9, 1931.

period August 27 to September 9. These sizes have not been affected by a second moult. Since all sizes smaller than 29 cm. should reach the hard-shelled condition after the first moult more quickly than the 29 cm. lobster, and yet the shell condition in these new-shelled males in the period August 27 to September 9 increased from 30.7 per cent with hard shells at 24 cm. to 69.2 per cent at 28 cm., we must conclude that the sizes 24 to 28 cm. have probably been affected in gradually decreasing degree by the second moulting. The percentage of the new-shelled lobsters at any given size with hard shells may be lowered in two ways, (a) by the lobsters of a certain size moulting so that the number of hard-shelled lobsters

of that size is reduced, and (b) by moulting at smaller sizes producing lobsters which fall into a higher size group. Growth experiments in 1932 at Pointe du Chêne indicate an approximate growth at a moult of 13 to 11 per cent for male lobsters between 20 and 25 cm. Thus since shell condition in 29 cm. males was not affected by this moulting, no second moulting took place at 28 and 27 cm. and probably little or none above 26 cm. However, since moulting produced new-shelled lobsters large enough to affect the 27 and possibly the 28 cm. class,

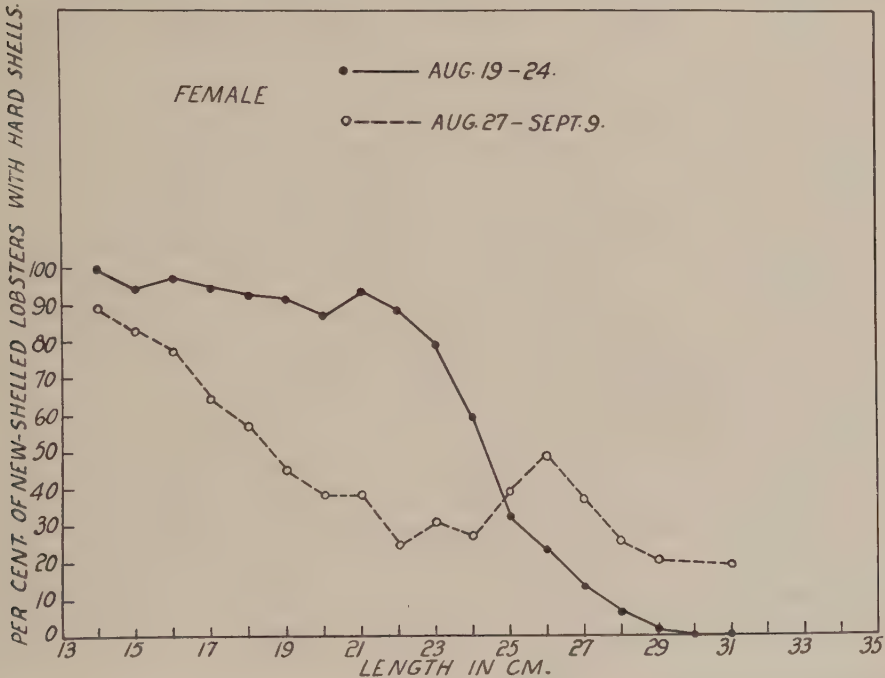


FIGURE 7. Percentage of new-shelled female lobsters of different sizes with hard shells in catches of 4555 lobsters in the Pointe du Chêne and Summerside area from August 19-24 and of 3720 lobsters in the same area from August 27-September 9, 1931.

some second moulting probably occurred as high as 25 cm. This corresponds exactly with the records of new-shelled lobsters preparing for moulting (see table VIII, male, column M) which give a small percentage of new-shelled males of 25 cm. preparing for moulting and none above 25 cm.

Second moulting of females, 1931 (Figure 7, tables VII and VIII). In the Pointe du Chêne and Summerside area, 1931, an examination of the shell condition of lobsters during the period August 27 to September 9 showed that at all sizes below 25 cm. the percentage of hard-shelled specimens among the new-shelled lobsters was considerably less than in the same area on August 19 to 24. It has already been shown that this effect could only have been produced by a second moult.

The decrease in the percentage of hard-shelled specimens among the new-shelled lobsters was greatest at 22 cm., at which size the proportion with hard

shells declined from 88.4 per cent on August 19 to 24 to 24.7 per cent during the period August 27 to September 9. Toward the sizes below 22 cm. during the period August 27 to September 9 there was a progressive increase in the percentage of the new-shelled lobsters with hard shells, with decrease in size, presumably owing to a quicker recovery from the second moult at these sizes.

Among the lobsters examined from August 27 to September 9, at 23 and 24 cm., there was a smaller percentage of hard-shelled specimens among the new-shelled lobsters than on August 19 to 24. At larger sizes the percentage of new-shelled lobsters with hard shells gradually increased until at 26 cm. the percentage with hard shells was 25.2 per cent greater than on August 19 to 24, at 27 cm. it was 23.4 per cent, at 28 cm. 19.7 per cent, and at 29 cm. 18.1 per cent greater than on August 19 to 24. Thus beginning with 26 cm. no factor except a gradual hardening of the shell was evident, this hardening having been progressively slower at the larger sizes. The 26 cm. females, therefore, have not been affected through having soft-shelled lobsters introduced among them by an increase in length of smaller lobsters by the second moulting, while all previous sizes have. Since the growth per moult of females between 20 and 25 cm. at Pointe du Chêne ranges from 11 to 7.5 per cent, 24 and 25 cm. females have not moulted a second time. This is confirmed by the fact that no new-shelled female lobsters above 22 cm. were recorded as preparing for moulting during the period August 27 to September 9 (table VIII, female, column M).

1932. In 1932 at Pointe du Chêne during examination of 4,291 lobsters at Pointe du Chêne and Summerside, from August 24 to September 29, male lobsters as large as 23 cm. and female lobsters of 21 cm. were found preparing for a second moult, their new and thin shells showing that they had already moulted once in the early summer, but no larger new-shelled lobsters preparing for moulting were observed although by the end of the period of observation moulting had almost completely ceased.

The completeness of the second moult

At the largest sizes preparing for a second moult there would be little moulting and it is only at several sizes below this maximum that a great amount of moulting takes place. In a lobster which has recently moulted the band of setae fringing the telson is a brilliant red for the first half of its length. The outer half is light in colour. In a freshly moulted lobster the line between these two bands of colour is very definite and distinct. Gradually, however, the brilliancy of the red band fades, the light band becomes dirtier and the distinct division between the two bands is lost, one gradually fading into the other. It is thus possible to separate hard-shelled lobsters which have recently moulted, say 2 weeks to 1 month previously, from hard-shelled lobsters which moulted 2 months or more previously. Using this method for lobsters below 23 cm. it was found that the lobsters below 23 cm. that had not moulted recently or were not preparing to moult for a second time amounted to 1.4 per cent. in Pointe du Chêne catches of 1,676 lobsters on September 16 to 18, 1931, and 6.4 per cent in Pointe du Chêne catches of 469 lobsters, September 28-29, 1932.

Other areas

The two moultings per year among the small lobsters of commercial size occur throughout the whole of western Northumberland strait, with the possible exception of the deep water fishing grounds off West point at the western end of the strait and off cape Tormentine at the eastern end of the western strait. These areas were not studied intensively enough to reach definite conclusions. Our observations show that some second moulting certainly takes place in these two areas among the smaller lobsters but the extent of the moulting has not been determined.

Magdalen islands. In the Magdalen islands information on the number of moults among commercial lobsters during the year has been obtained from tagging operations. 629 male and 84 female lobsters caught in House Harbour lagoon, Magdalen islands, from July 10 to August 10, 1931, were tagged and liberated immediately in House Harbour lagoon or in Pleasant bay. These were all new-shelled lobsters which had moulted once since winter. In the liberation areas fishing had ceased in 1931 before liberation of the tagged lobsters. 46 of the tagged lobsters were caught in May and 3 in June, 1932. 558 males between the sizes 23 and 35 cm. were tagged and 46 tags returned, or a return of 8.2 per cent. 71 males of 17 to 22 cm. were tagged but no returns were obtained. Among the females 3 returns were obtained from the tagging of 56 lobsters between 23 and 30 cm. or a percentage return of 5.4, while from the tagging of 28 female lobsters 18 to 22 cm. in length no returns were obtained. Practically all the above recaptures from the tagging in July and August 1931 were in May, 1932. Lobsters were marked by a metal tag through the telson. May is much too early for moulting to have taken place in 1932 and the failure to get any return from the small lobsters of less than 23 cm. tagged indicates that these small lobsters moulted during the late summer or fall of 1931 and thus lost their tags with the old shell.

Grand Manan. Special fishing at Grand Manan in 1932, even when traps fully capable of catching small lobsters were used, failed to disclose the presence of any significant number of lobsters below 18 or 19 cm. in this area. Moreover, the first moult among the Grand Manan lobsters only takes place in late August and September, at about the same time that the second moult among the smaller commercial lobsters is taking place in western Northumberland strait. Thus it is practically certain that even among the smallest commercial lobsters at Grand Manan there is only one moult during the year.

DISCUSSION AND CONCLUSIONS

From the above data it would appear that moulting in the regions examined occurs earliest in Malpeque bay and the lagoons of the Magdalen islands where a great part of the moulting is over by the end of June. In Shediac bay, western Northumberland strait, in 1932, moulting began about July 6, and by July 20, 91.5 per cent of the lobsters caught had recently moulted. In Pleasant bay, Magdalen islands, 1931, moulting began about July 8 and it was not until July 31 that the percentage of new-shelled lobsters was similar to that obtained in Shediac

bay, 1932, on July 20. At Seal cove, Grand Manan, the first moulting period was latest, beginning about August 15 and probably reaching its maximum in September.

Table IX gives the comparative bottom temperatures obtained during experimental fishing on the above lobster fishing grounds. The Malpeque bay temperatures have been kindly provided by Dr. Needler. The Malpeque bay temperature station is about $1\frac{1}{2}$ miles ($2\frac{1}{2}$ km.) south of the fishing point at Hog island reef, but the depths in the two areas are approximately the same.

TABLE IX. Bottom temperatures in degrees Centigrade in areas where experimental lobster fishing was carried on in 1931 and 1932.

Date	Malpeque bay 11 m.	House har. lagoon Mag. Is. 1-1½ km. northeast of Red I. 8-11 m.	Meule rock Mag. Is. 5/8 km. off cape Meule 8 m.	Near wharf at cape Meule 40 m. off- shore	Malpeque bay 11 m.	Medea rock Shediac bay 7½-9 m.	Long Pond bay Grand Manan middle of bay 200-300 m. offshore 4-8 m.
	1931	1931	1931	1931	1932	1932	1932
June 29					17.79		
" 30							
July 1							
" 2	13.8						
" 3							
" 4						13.2	
" 5							
" 6						14.3	
" 7			12.3				
" 8			12.1		16.80	13.8	
" 9			14.94				
" 10		16.44	12.86				
" 11	18.1						
" 12						14.6	
" 13		18.76					
" 14		15.08	10.39				
" 15		14.17	13.23		17.83		
" 16		15.11				16.1	
" 17							
" 18	17.1					15.4	
" 19							
" 20		16.83	15.7	16.03			
" 21					17.61		
" 22		18.06					
" 23		18.80					
" 24		19.24	16.76				
" 25	20.23	20.00	15.60	16.35			
" 26							
" 27		17.33					
" 28		18.09	15.50	14.92	19.20		
" 29							
" 30							
" 31		17.95	14.56	15.70			
Aug. 1							
" 2							
" 3		17.26					
" 4	21.42						
" 5		17.47					10.5
" 6		18.4					10.54
" 7		18.38					
" 8							
" 9							
" 10	19.18						10.9
" 11							
" 12					19.40		10.6
" 13							
" 14							
" 15							11.4
" 16							
" 17	19.53						
" 18					19.70		
" 19							
" 20							

The remaining temperatures were taken on the fishing areas during the experimental fishing by which the times of moulting were compared. The time of the first general moulting is apparently directly correlated with the temperature of the water during the summer. The highest bottom temperatures were found on the fishing grounds in Malpeque bay, and in House Harbour lagoon, Magdalen islands, where also occurred the earliest moulting. Early summer temperatures on the inshore fishing grounds in Pleasant bay, Magdalen islands, and in Shediac bay, western Northumberland strait, were several degrees lower and the moulting period several weeks later than in Malpeque bay, or House Harbour lagoon. The slightly higher temperature on the fishing ground in Shediac bay than in Pleasant bay is reflected in the slightly earlier moulting in Shediac bay. The lowest summer temperatures were found at Grand Manan where temperatures about 8°C. lower than in Malpeque bay were found in August, 1932. Correlated with this the first general moulting period at Seal cove, Grand Manan was over two months later than in Malpeque bay. It appears that for each degree centigrade lower summer temperature the first general moulting period for the year is postponed for roughly a week or more.

Why this correlation of moulting with summer temperature, and what influence if any have winter temperatures? Cobb (1901), says "the experience of lobster pounds has shown that the quantity of food required depends largely on the temperature of the water, as the lobsters do not eat as freely when the water is cold as in water of a higher temperature." Herrick (1896) records "that at the lobster pound at Southport, Maine, they do not feed the lobsters after the first of December, although lobsters are retained in the pound until March." During the winter the whole gulf of St. Lawrence is covered with ice and it is probable that the water in the whole of the shallower parts of the gulf area during the winter reaches a temperature at which little or no digestion or tissue growth occurs. During the winter in the Grand Manan area the water is slightly warmer than in the gulf and the trapping of small quantities of lobsters in deep water indicates that some digestion is probably going on in the offshore parts of this area at least. This should produce a slight tendency toward earlier moulting at Grand Manan than in gulf areas. The early warming up of the southern gulf areas in late spring and in summer to a point many degrees higher than at Grand Manan, apparently speeds up the rate of digestion in the southern gulf so much that the slight advantage obtained by the Grand Manan region during the winter is entirely overcome and moulting occurs much earlier in the southern gulf regions than at Grand Manan.

Such direct correlation between time of moulting and summer temperature exists in the above areas that the presence of more food in one area than another is probably a very small factor in determining the time of moulting. It would seem probable that owing to the scavenging habits of the lobster and its dependence on slow moving or fixed bottom forms, it is generally able to obtain so much food that the differences between areas in this respect would not significantly influence the time of moulting.

Number of moultings. In the areas with a high summer temperature, such as western Northumberland strait and the lagoons of the Magdalen islands, the

first moulting period occurs so early that among the fast-growing smaller lobsters of commercial size a second moulting may occur before the cooling of the water in the fall. In these areas nearly all the lobsters of commercial size below 23 cm. moult twice during the year. Female lobsters in western Northumberland strait have an upper limit for second moulting several centimetres below that of the male. The largest females found actually preparing for a second moulting in 1931 were 22 cm. in length and in 1932, 21 cm., while in the same years respectively, males as large as 25 and 23 cm. were preparing for a second moulting.

In the Grand Manan area the much lower summer temperature retards the first moulting period so much that in all probability no second moult can take place even among the smallest commercial lobsters.

LENGTH INCREASE ON MOULTING

INTRODUCTION

Measurements of lobsters before and after moulting were obtained at Pointe du Chêne and at Grand Manan in 1932. Lobsters preparing for moulting and which would moult in a few days were placed in crates and allowed to moult, after which the lengths of the old and of the new carapace were measured. The carapace measurement was taken from the bottom of the eye-socket directly back in a line parallel to the median dorsal line. The carapace measurement

TABLE X. Comparison of percentage increase in length on moulting of individual lobsters as calculated from total length and from carapace measurements before and after moulting. Lengths in centimetres.

Sex	Total length				Carapace length		
	Before moulting	No. of days before moulting measurement taken	After moulting	Per cent increase	Before moulting	After moulting	Per cent increase
♀	14.4	3	16.65	15.6	4.79	5.60	16.9
♀	14.9		16.6	10.1	5.00	5.7	14.0
♂	15.05	8	17.6	16.9	5.28	6.15	16.5
♀	15.2		16.7	9.9	4.96	5.59	12.7
♂	15.5	3	17.4	12.3	5.15	6.1	18.4
♀	21.3		22.9	7.5	7.55	8.35	10.6
♂	21.6	8	23.4	8.3	7.55	8.4	11.3
♂	22.4		24.4	8.9	7.90	8.7	10.1

gives a better indication of the true growth on moulting than does the total length measurement since as shown in table X, the increase on moulting as calculated from total length measurements is generally less than that calculated from carapace (eye-socket back) measurements. The old shell of the lobster just previous to moulting is filled with meat and a certain amount of stretching occurs, especially at the junction of thorax and abdomen during several days immediately preceding moulting. For this reason increases judged from total length

measurements taken a few days before and after moulting are unsatisfactory since the calculated growth is too low. Thus carapace measurements only have been depended on. (The one case in table X where the percentage increase as judged by total length was not less than that judged by carapace length, occurred when the lobster was measured 8 days before moulting.)

Table XI shows the rapidity with which the new size was assumed after moulting in the case of 4 lobsters. Carapace measurements taken immediately after moulting were low, but within 35 minutes or less to 1 hour after moulting the carapace had stretched to the full size. Total length measurements usually were constant within 2 or 3 hours after getting out of the old shell. In from 2½ to 4 hours the claws filled out. No further increase either in carapace length or in total length occurred even if as in one case the lobster was kept and fed for 13

TABLE XI. Time of attaining full size after moulting, 1932

Designation of lobster	Sex	Locality	Time since moulting	Total length new shell (cm.)	Carapace length new shell (cm.)	% increase in length on moulting (carapace)	Condition of big claws
B	♂	Grand Manan	2 hr.		13.1	11.49	Claws ½ filled out
			3 days	35.5	13.1	11.49	
			5 days	35.5	13.1	11.49	
C	♀	Pte. du Chêne	5 min.	18.7	6.58	10.03	Claws shrivelled
			1 hr.	19.0	6.68	11.71	Claws ¾ filled out
			2 hr. 35 min.	19.5	6.67	11.54	Claws filled out
			3 hr. 50 min.	19.5	6.68	11.71	
			27 hr.	19.4	6.68	11.71	
D	♂	Pte. du Chêne	5 min.	21.5	7.73	14.01	Claws ½ filled out
			1 hr.	22.0	7.85	15.78	Claws ¾ filled out
			2 hr.	22.4	7.84	15.63	Claws nearly filled out
			2 hr. 40 min.	22.4	7.83	15.49	Claws almost completely filled out
			13 days	22.4	7.83	15.49	
E	♂	Pte. du Chêne	3 min.	29.8	11.30	9.71	Claws shrivelled
			35 min.	30.1	11.40	10.68	Claws ½ filled out
			4 hr. 20 min.	30.6	11.37	10.39	Claws almost fully filled out, slight lateral wrinkles in claws not yet ironed out

days after moulting. Since our measurements have shown that the carapace length in rubber- and in buckle-shelled lobsters bears the same relation to the total length as in old-shelled lobsters (unpub. MS.), the total length of the lobster does not increase between moults except, as indicated by table X, slightly during several days immediately preceding moulting.

In measuring new-shelled lobsters to calculate growth the lobster was not measured until the claws had lost their shrivelled appearance and had filled out. As shown in table XI, this would occur several hours after the carapace had attained its full length. Usually, however, from 6 hours to 2 days would elapse after moulting before the new-shelled lobster was measured. Thus all new-

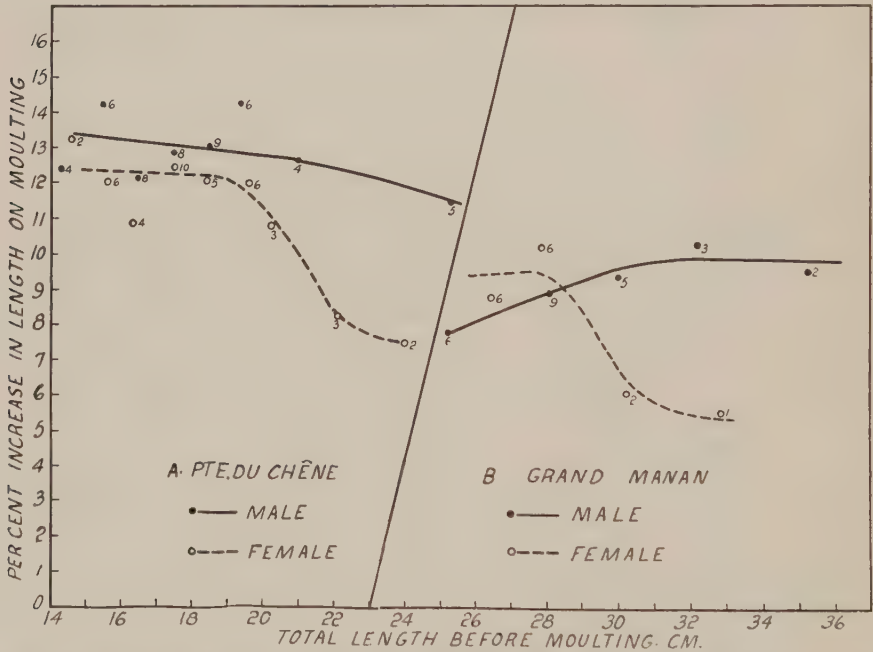


FIGURE 8. Percentage increase in length on moulting of 50 male and 41 female lobsters at Pte. du Chêne, August and September 1932, and of 25 male and 15 female lobsters at Grand Manan, August, 1932. (Numbers represent the number of specimens from which the average positions of the points shown were calculated.)

shelled lobsters had stretched to their full new size before being measured. In comparing growth in various areas only lobsters which possessed normal claws both in the old-shelled and in the new-shelled condition will be considered.

NORMAL GROWTH AT POINTE DU CHÊNE

During the fall season of 1932, lobsters which were prepared to moult and which would have moulted within several days were obtained directly from the fishing grounds and allowed to moult in crates at Pointe du Chêne. Figure 8A shows the average growth on moulting of 50 male and 41 female unmutilated lobsters from August 29 to September 30. The amounts of growth of the differ-

ent lobsters were very variable, lobsters of the same size and sex growing by such different amounts at a moult as 9.1 per cent. and 17.1 per cent. The growth of the male on moulting decreased very slowly from 13.4 per cent at 14.5 cm. to 11.5 per cent at 25 cm. The percentage growth on moulting of the female was at the smaller sizes not much different from that of the male but began to decrease rapidly between 19 and 20 cm., this decrease continuing until at 22 cm. the female growth on moulting was only 8.5 per cent. After the sharp drop between 19.6 and 22.1 cm. the percentage growth of the female on moulting did not decrease so rapidly and the curve flattens out again. Unfortunately, no moulting females larger than 24 cm. could be obtained.

Some lobsters caught on Medea rock, Shediac bay, during special fishing at Pointe du Chêne in July, 1932, were provided with abundant food until ready for moulting. The average growth on moulting of 5 male lobsters between 14 and 22 cm. was 13.4 per cent, as compared with an average of 13.1 per cent for 44 male lobsters between the same sizes during the fall moult. The average growth on moulting of 8 female lobsters between 15 and 21 cm. in July was 12.4 per cent, as compared with an average of 12.0 per cent for 34 female lobsters between the same sizes during the fall moult. At the above sizes the July moult was the first moult since winter and the August to September moult the second.

GROWTH AT WOODWARDS COVE POUND, GRAND MANAN, 1932

At Grand Manan it was impossible to obtain lobsters preparing for moulting directly from the fishing grounds, and lobsters in this condition were obtained from Woodward's cove pound from August 13 to 18. The lobsters in this pound were obtained from the area between Cape Sable and Grand Manan, most of the lobsters being obtained from the Grand Manan area. The lobsters used in the growth experiments had been in the pound from 2 to 5 months and attempts had been made to feed them well during this time. Figure 8B gives the curves of average growth on moulting obtained from measurements of 25 males and 15 females. The graph shows in the case of the male a low growth on moulting of only 7.8 per cent at 25 cm., rising to 9.8 per cent at 32 cm. and remaining as high as 9.6 per cent at 35 cm. The growth of the female on moulting was not greatly different from that of the male at the sizes 25 to 28 cm. At larger sizes the growth per moult of the female becomes considerably less than that of the male.

GROWTH AT POINTE DU CHÊNE OF LOBSTERS KEPT IN FLOATS

From June 28 to July 20, 1932, the growth on moulting of 64 male and 55 female unmutated lobsters obtained from the lobster retaining floats at Pointe du Chêne was determined. These lobsters had been caught on the northern New Brunswick coast from Burnt Church to Richibucto, and in northwestern Prince Edward Island. No lobsters were placed in the floats after July 1. The small lobsters in the floats received little or no food and the larger lobsters (over 23 cm.) received a little food. The lobsters whose growth on moulting was measured had been from 1 day to about 6 weeks in these floats before moulting.

In figure 9A the growth on moulting of the males and in 12B the growth on

moulting of the females obtained from these floats is compared with the normal growth on moulting at Pointe du Chêne of male and female lobsters which have gone through their preparations for moulting on the fishing grounds and moulted several days after capture. It is noticed that the growth on moulting was considerably less in the case of the lobsters from the floats, which had not received their normal supply of food.

DISCUSSION AND CONCLUSIONS

The normal percentage growth of the males on moulting seems to decrease gradually from the smaller toward the larger sizes. Why then the low growth on moulting of the smaller sized lobsters obtained from the Woodward's cove

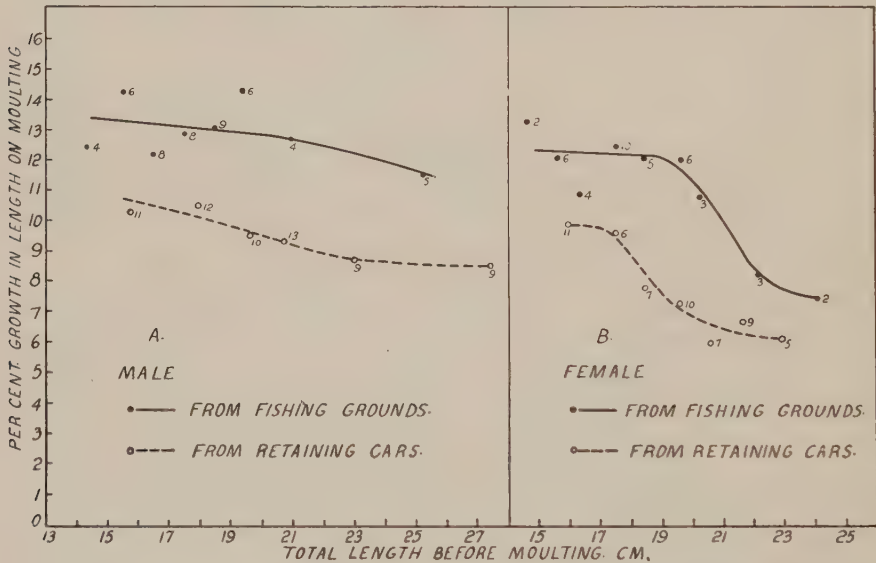


FIGURE 9. Percentage increase in length on moulting of 50 male and 41 female lobsters obtained several days before moulting directly from the fishing grounds of Pte. du Chêne, August-September 1932, compared with that of 64 male and 55 female lobsters obtained from the retaining cars at Pte. du Chêne June-July 1932. (Numbers represent the number of specimens from which the average positions of the points shown were calculated).

pound, Grand Manan? The only explanation that suggests itself is that in the limited area of the pound where the food supply was intermittent and localized in small areas, the larger lobsters may have exercised control and received relatively much more food than the smaller sizes. This would lead to a smaller percentage growth on moulting at the smaller sizes.

Hadley (1906), and Herrick (1911), have assumed that the growth of the female on moulting was essentially the same as that of the male both before and after maturity. Their data on sizes above sexual maturity, however, were very scanty. The pre-mature growth on moulting seems to be approximately similar in males and females. If there is a definite difference more measurements will be needed to determine it. Between 20 and 22 cm., however, at Pointe du

Chêne and between 28 and 30 cm. at Grand Manan, a very sharp decrease occurs in the percentage growth of the female on moulting. The smallest sexually mature female obtained at Pointe du Chêne was 18.0 cm. long while the smallest at Grand Manan was 34.6 cm. The average size at first sexual maturity in both places would probably be several centimetres larger. Thus the sharp drop in the percentage increase in size of the female on moulting can be correlated with the onset of maturity in different regions when a large amount of the food digested must be used to nourish the developing eggs. At this time the body of the lobster, exclusive of the ovaries, can be considered as undernourished as compared with its immature stage and thus the lobster does not grow so much on moulting. The sudden decrease in percentage growth on moulting of the female between 28 and 30 cm. obtained at Grand Manan occurs at a smaller size than would be expected from the size at first maturity on the fishing grounds in this area. The lobsters in Woodward's cove pound, however (from which the Grand Manan results were obtained), were collected in part from western Nova Scotia west of Cape Sable where the smallest size at maturity is several centimetres below that at Grand Manan. The bottom water in the pound in August also averaged 1 or 2°C. higher than on the fishing grounds outside the pound and this would work toward maturity at a smaller size with a consequent decrease in the percentage growth of the female on moulting. After the rapid decrease in percentage growth on moulting at the onset of sexual maturity, the curve showing the percentage growth of the females flattens out and while more data are still required it is probable that the rapid decrease in percentage growth on moulting of the female on the approach of maturity passes with still further increase in size into a much more gradual decline in percentage growth on moulting. At Pointe du Chêne the greatest percentage growth on moulting was obtained when lobsters ready for moulting were obtained directly from the fishing grounds, or when lobsters obtained from the fishing grounds were supplied with abundant food until ready for moulting. Lobsters do not eat much during the week previous to moulting and it is almost impossible to trap them in quantities at this time. Thus keeping lobsters in crates without food for several days before moulting should not measurably affect growth and such growth can be regarded as normal. When, however, the lobsters used for growth determination have been kept in aquaria, floats, or pounds, the growth cannot be considered as normal, and if as occurred at the Pointe du Chêne floats in June to July, 1932, the lobsters were underfed or not fed, the percentage growth on moulting decreases.

From the results obtained the growth of the smaller lobsters at Pointe du Chêne during the first moult since winter, in July, seems to be approximately the same as during the second moult in late August and early September. However, the number of lobsters measured at these sizes during the first moult (13), only allows an approximate comparison.

The growth on moulting of the lobsters in the Woodward's cove pound at Grand Manan is probably a little below that on the fishing grounds in this region, and it is probable that the females between the sizes of 18 and 24 cm. grow much more on moulting on the Grand Manan fishing grounds than females of corres-

ponding size at Pointe du Chêne (18 and 34 cm. are approximately the smallest sexually mature sizes at Pointe du Chêne and Grand Manan respectively).

RELATIVE NUMBERS OF MALE AND FEMALE LOBSTERS AT DIFFERENT SIZES

Measurements of male and female lobsters were taken in 1930, 1931, and 1932 along most of the coast of the Maritime provinces. All measurements considered in the following are of spring and early summer catches of old-shelled, hard-shelled lobsters. No late summer or fall catches are included since differing conditions of shell in male and female lobsters for a month or more after the moulting period results in differential capture. The measurements do not include egg-bearing females. In almost all cases the entire number of lobsters caught by a fisherman during a day's fishing was measured, and in the remaining meas-

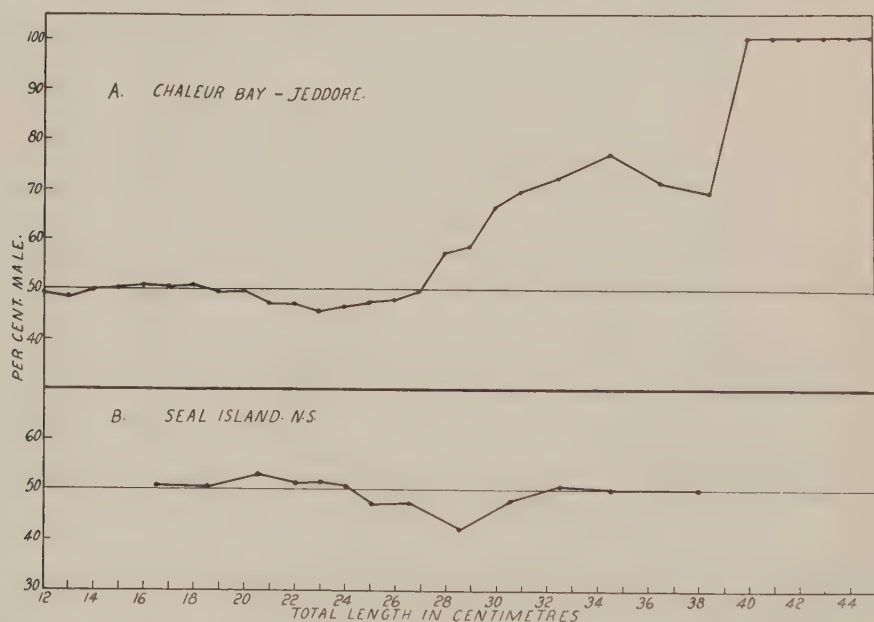


FIGURE 10. Percentage of males at different sizes in measurements of 68306 old-shelled lobsters in the region from Chaleur bay to Jeddore, June and July 1930-1932 and in 2938 lobsters from Seal island in southern Nova Scotia May 22-25, 1931.

urements the only division was that by the fishermen or the buyers themselves into large (over 23 cm.) and small (under 23 cm.) so that there was no selection for sex.

Chaleur bay to Jeddore. Figure 10A and table XII show the percentage of males at different sizes in measurements of 68,306 lobsters in localities ranging from Chaleur bay to Jeddore in Halifax county, N.S., including the Magdalen islands, Prince Edward Island and eastern Cape Breton (western Northumberland strait, measurements of male and female lobsters which were taken after the moulting period, with many of the lobsters in the soft-shelled condition, are not

TABLE XII. Measurements of male and female lobsters in the region from bay Chaleur to Jeddore, June and July, 1930-32

Total length (cm.)	Male	Female	Total	Percentage male	Excess male	Excess female
12	34	35	69	49.5		1
13	249	265	514	48.4		16
14	858	859	1717	50.0		1
15	1991	1975	3966	50.2	16	
16	3292	3185	6477	50.8	107	
17	4301	4211	8512	50.5	90	
18	4584	4401	8985	51.0	183	
19	4161	4204	8365	49.7		43
20	3533	3579	7112	49.7		46
21	2635	2919	5554	47.4		284
22	2080	2332	4412	47.1		252
23	1597	1885	3482	45.9		288
24	1253	1429	2682	46.7		176
25	903	998	1901	47.5		95
26	637	691	1328	48.0		54
27	513	515	1028	49.9		2
28	412	306	718	57.4	106	
29	275	194	469	58.6	81	
30	247	125	372	66.4	122	
31	146	64	210	69.5	82	
32	92	48	140	72.1	44	
33	76	17	93		59	
34	64	17	81	76.9	47	
35	36	13	49		23	
36	13	7	20	71.1	6	
37	14	4	18		10	
38	4	2	6	69.2	2	
39	5	2	7		3	
40	5		5	100.0	5	
41	6		6	100.0	6	
42	3		3	100.0	3	
43	3		3	100.0	3	
44	1		1	100.0	1	
45	1		1	100.0	1	
Total.....	34024	34282	68306		1000	1258

included, and no measurements of male and female lobsters were made in western Cape Breton). The area under consideration will, in further discussion, be called the "Chaleur bay to Jeddore" area. This area forms a unit in one respect at least, since throughout its whole range berried lobsters as small as 18 to 21 cm. probably occur (see figure 4). In figure 10A the graph is indefinite at sizes from 12 to 14 cm. at which sizes few lobsters were obtained. From 14 to 18.8 cm. more males than females were caught; from 18.8 to 27 cm. more females than males and at all larger sizes more males than females. At these larger sizes the

percentage of males in the catch rapidly increased until at the largest sizes 100 per cent. were males. As seen in table XII, however, at these large sizes there were very few lobsters.

Southwestern Nova Scotia. Figure 10B and table XIII give measurements of 2,938 lobsters at Seal island at the southwest corner of Nova Scotia. At sizes from 16.5 to 24.2 cm. there were more males than females in the catch, from 24.2 to 32.0 cm. more females than males, and above this approximately an equal number of males and females. The essential points of difference between this curve and that of the "Chaleur bay to Jeddore" area are the change from a greater proportion of males to a greater proportion of females which occurs in the graph of the "Chaleur bay to Jeddore" region at 18.8 cm. and in that of the Seal island area at 24.2 cm., and the presence of almost equal numbers of males and females at the largest sizes caught at Seal island.

TABLE XIII. Measurements of male and female lobsters captured approximately 2 to 10 miles (3-15 km.) off Seal island, N.S., May 22-25, 1931

Size cm.	Male	Female	Total	Per cent male
14	1		1	
15	4	4	8	
16	30	33	63	50.8
17	90	83	173	
18	119	125	244	
19	159	148	307	50.5
20	158	160	318	
21	171	132	303	53.0
22	131	125	256	
23	101	96	197	51.2
24	102	99	201	51.3
25	75	84	159	50.7
26	67	78	145	47.2
27	61	64	125	47.4
28	43	58	101	
29	32	45	77	42.1
30	36	35	71	
31	21	27	48	47.9
32	19	18	37	
33	13	13	26	50.8
34	10	13	23	
35	11	8	19	50.0
36	8	4	12	
37	7	7	14	50.0
38	2	3	5	
39	1	0	1	
40	0	4	4	
	1472	1466	2938	

DISCUSSION AND CONCLUSIONS

Apparently the numbers of males and of females in the lobster population are approximately equal and the male and female differential mortality from natural causes very small since in measurements of 68,306 lobsters from the "Chaleur bay to Jeddore" area, 34,024 were male and 34,282 female and in measurements of 2,938 lobsters from the Seal island fishing grounds, there were 1,472 males and 1,466 females. Thus we need not consider the possibility of inequalities in the natural sex ratio producing some of the above variations.

Both in figures 10A and 10B there is an early period when more males are caught than females. This occurs between 14 and 18.8 cm. in the "Chaleur bay to Jeddore" area and between 16.5 and 24.2 cm. at Seal island. Lobsters are immature at these sizes in the respective areas. For these immature lobsters it is doubtful whether any difference in growth exists among males and females. Thus since the male and female sex ratio seems to be equal we can assume an approximately equal number of males and females in the population at these sizes, more males being caught because of a presumed greater activity of the males. There is some evidence that such greater activity exists. MacClement gives the following account of the relative activity of male and female lobsters in the Long Beach lobster pond in Nova Scotia in 1917. The relative activity was judged by the number of each sex entering traps placed in various parts of the pond, which contained 1,000 lobsters of each sex 25.4 cm. or over in length. The size at which sexual maturity was attained was over 30 cm. as determined by the size of lobsters extruding eggs in the pond; and three-quarters of the lobsters in the pond were immature. During July, August and September, 2,169 males were trapped and 1,729 females, so that the activity of the males was 25 per cent. greater than that of the females (unpub. MS.).

In the "Chaleur bay to Jeddore" area a greater number of females than males are caught between the sizes of 18.8 and 27.0 cm. This may be due to a combination of two factors. The catching of more males than females at the smaller sizes would of itself leave more females in the population at larger sizes, also in this region the smallest sizes at first maturity range from 18 to 21 cm., and as shown in figure 8 the female lobster grows considerably less at a moult than the male on approaching sexual maturity. As a result of this a greater number of year classes of females than of males are included among the early mature sizes and at these sizes more females than males appear in the catches. (No females carrying eggs are included in the above measurements so that the disturbance in the comparisons drawn between the numbers of male and female lobsters due to the fishermen's returning berried lobsters to the sea is lessened. Berried females returned to the sea in previous years and not carrying eggs at the time of measurement, thus being included in the above catches, should be roughly compensated for by the females carrying eggs at the time the measurements were taken and thus not being included in the above comparisons of males with non-berried females.) In the Seal island measurement (figure 10B) more females than males appear in the catches between 24.2 and 32.0 cm. In figure 8B the rapid slowing down of the percentage growth of the female on moulting below

that of the male begins at about 28.5 cm. in lobsters gathered in various areas from Seal island, N.S., to Grand Manan. The smallest egg-bearing lobsters found at Seal island were 32 cm. long and although it would doubtless be possible to secure berried lobsters several centimetres smaller from this area, the region is essentially one of late sexual maturity (see figure 4). In figure 10B, therefore, showing the Seal island catch, the change to a greater proportion of females in the catch seems to occur at too small a size to be caused by a slowing down in the growth rate of the female on the approach of sexual maturity. However, the early period during which more males are caught than females extends over a much longer range of sizes at Seal island (7.5 cm.), than in the "Chaleur bay to Jeddore" area (4.5 cm.), and it is probable that the male population is finally reduced to the point where, in spite of a greater percentage of the male population being caught than the female, the total number of females caught at 25 cm. is greater than the number of males. At larger sizes the slowing of the growth rate of the female as compared with that of the male would help to keep the catch of females in excess of that of the males and this continues in the Seal island catch until 32 cm. as compared with 27 cm. in the "Chaleur bay to Jeddore" measurements.

Finally in the area from Chaleur bay to Jeddore, at all sizes larger than 27 cm. a greater number of males are caught than females. Since females after the onset of maturity grow more slowly than males, the males at all these larger sizes are considerably younger than females of corresponding size and consequently have run less risk of being captured in fishermen's traps. Consequently, more males than females have escaped to reach the larger sizes. In the Seal island measurements in southern Nova Scotia this final increase in the relative number of males to females at the larger sizes is not evident. In this region the slowing down of the growth rate of the female compared with that of the male occurs much later than in the "Chaleur bay to Jeddore" area, and consequently the size at which more males are caught than females should be also greater. It is probable that if less intensive trapping allowed the attainment of still larger size than is represented in the Seal island catches, the greater proportion of the largest would be males.

AVERAGE SIZE

Average sizes were obtained from measurements of lobsters in 1930, 1931 and 1932. Measurements were taken in centimetres from the tip of the rostrum to the end of the telson. On the measuring board used the first space measured $1\frac{1}{2}$ cm. and the remaining spaces 1 cm. each. The spaces were numbered consecutively. In measuring, anything falling, for example, in the 22 cm. space was recorded as 22 cm. in length. If the end of the telson reached the line separating the spaces 22 and 23 the length recorded was 23 cm. Lobsters were in nearly all cases measured alive. In measuring, the lobster was laid on its back on the board and the thumbs placed between the third and fifth walking legs. If placed on the board in this way the lobster straightens itself perfectly and the length is read off. In measuring lobsters to the nearest centimetre the usual assumption was made that in dealing with large numbers of individuals the variations on one

side of the middle of the centimetre spaces would be approximately equal to the variations on the other.

The method of sampling was to take the whole day's catch from as many fishermen as possible, from 4 to 10 catches being usually measured in each place. The lobsters of each fisherman would be obtained from 100 to 300 traps, usually scattered over a wide area of fishing ground. In all 119,645 lobsters from such catches were measured in 161 localities or an average of 743 in each locality.

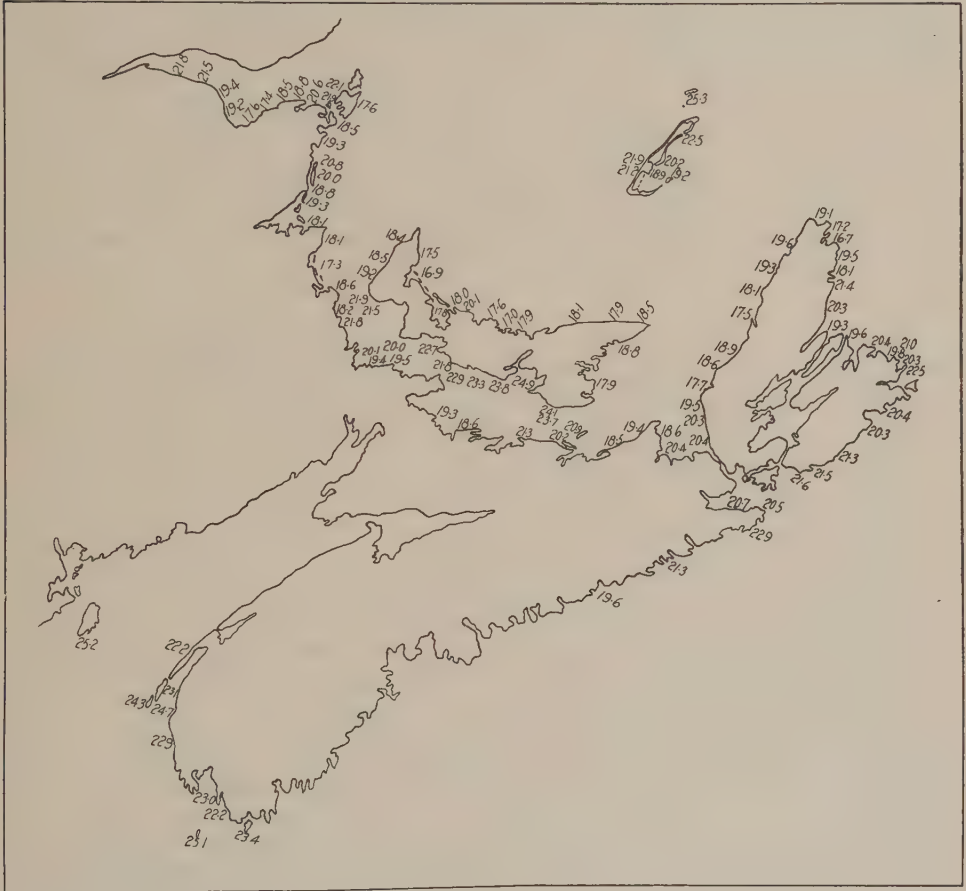


FIGURE 11. Average sizes in centimetres of lobsters in the commercial catches, as determined by measurements in 1930, 1931 and 1932.

Average sizes were determined statistically, the standard error ranging in most cases from .07 to .20 cm., the usual standard error being about .10 cm. (The chances are 68 in 100 that the obtained average does not deviate from the true average by more than $\pm$ or $-$ the standard error.)

Figure 11 shows the average sizes obtained on different parts of the Atlantic coast. In order to secure a uniform comparison, wherever possible the average sizes obtained by Professor A. F. Chaisson and by the writer in 1930 are used. The sizes in Prince Edward Island, except for the part fringing western North-

umberland strait, were obtained by the writer and Mr. R. V. V. Nicholls in 1931, and the eastern Nova Scotia at Liscomb and Port Dufferin and the Grand Manan averages by the writer in 1932. Duplicate measurements by the writer were also taken in western Northumberland strait in 1931 and 1932, and in the Magdalen islands and northeast Nova Scotia in 1931. The average sizes obtained from these measurements were essentially similar to those shown in figure 11.

Regional differences. In the whole gulf of St. Lawrence region from Chaleur bay to northern Cape Breton, including Prince Edward Island and the Magdalen islands, in eastern Cape Breton and the coast of Nova Scotia as far south as Port Dufferin, the average sizes of the commercial catch were as a rule small, usually ranging between 17.5 and 21 cm. (The only exceptional region of any extent in this area was the eastern part of the south coast of Prince Edward Island where the size, as a rule, ranged from 22 to 24.9 cm.) In southern Nova Scotia and Grand Manan the average size of lobsters in the fishermen's catches was much

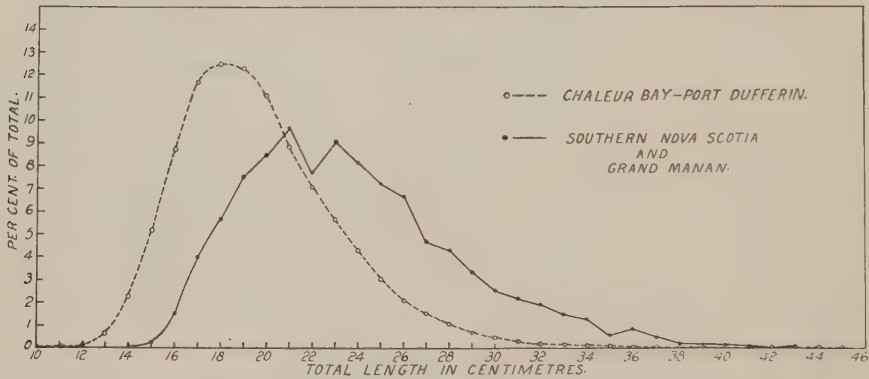


FIGURE 12. Percentage of lobsters of various sizes in a total catch of 83,117 lobsters in localities ranging from Chaleur bay to Port Dufferin, and of 6688 lobsters in southern Nova Scotia from Clarks harbour west and Grand Manan, 1930-1932.

larger than that usually found in the southern part of the gulf, ranging from 22.2 to 25.2 cm.

Figure 12 shows the percentage composition of the commercial catch in the above mentioned "Chaleur bay to Port Dufferin" and the "southern Nova Scotia and Grand Manan" regions. As in figure 11, duplicate measurements of lobsters in the same area in different years are not included. It will be noted that in the "Chaleur bay to Port Dufferin" region the smallest lobsters obtained in the commercial catch were 10 cm. in length, no significant numbers having been obtained before 13 or 14 cm., and the greatest amount of the fishing concentrated on sizes from 15 to 25 cm. In the "southern Nova Scotia and Grand Manan" area the smallest commercial lobsters were 14 cm. in length with no significant catch before 16 cm.; the intensity of fishing being spread over a much greater number of sizes than in the "Chaleur bay to Port Dufferin" region.

Local differences. In Chaleur bay, measurements were taken along the southern shore. The smallest average sizes were found on the eastern side of

Nipisiguit bay. Beginning at the bottom of Nipisiguit bay the average size gradually increased both toward the head and toward the mouth of Chaleur bay.

In Prince Edward Island the smallest average sizes were on the north side. Sizes on the western shore were a little larger, and on the south the average size increased from west to east until on the eastern part of the southern shore of the island the average sizes were 5 or 6 cm. larger than those usual on the north side.

The smallest average sizes in the Magdalen island area were found in Pleasant bay. The averages were larger both in the western and northern areas with the largest average size occurring at the most northerly fishing ground in the area, Brion island.

In eastern Cape Breton the smallest average sizes occurred at the north, the average size steadily increasing in spite of exceptions, toward the southern end of the island.

In the southern Nova Scotia and the southern New Brunswick area the largest average sizes were found at Seal island, at the mouth of St. Mary bay, in the nearby bay of Fundy region, and at Grand Manan.

DISCUSSION AND CONCLUSIONS

Average sizes such as given in figure 11 must necessarily be taken at different times in different places. Complications arise at once since, as some of our data show, the proportion of large lobsters in the catch as compared with small is greater during the early part of the open season than later. The proportions of large and small lobsters caught will also vary with the condition of shell, and with the year in which the measurements are taken. The errors due to these factors have been reduced as much as possible, first by taking all the measurements, except in western Northumberland strait, during the last month of the open season, and in the old shell condition, before moulting; and, secondly, by using in our comparison of averages in figure 11 mostly those obtained in the one year, 1930.

Many factors probably contribute to the differences in average size in various areas. Among them the following are in our opinion the most important. Limiting factors such as too low temperature might seriously decrease the percentage survival of the lobster fry in certain regions and such regions might be populated largely by lobsters which have migrated into it. Such lobsters will be on the average much larger than lobsters from an area where conditions are more suitable for breeding. An area in which successful survival in the larval stage provides greater numbers of young lobsters, can stand a large fishery and is fished more intensively than an area where less successful breeding conditions provide a scarcer supply. This again lowers the average size in an area with very successful breeding conditions. An area with shallow water and smooth bottom lends itself to much more intensive fishing than one with deep water and rough bottom since in the former more traps can be used and the traps fish more effectively. Differences also exist in the distance apart of the lower laths of the lobster trap, the range being from $\frac{3}{4}$ inch (2 cm.) in many parts of the gulf to $1\frac{1}{4}$ inches ($3\frac{1}{4}$ cm.) at Grand Manan. Thus in most of the gulf areas the smallest lobsters usually caught are 12 or 13 cm. long while in southern Nova Scotia the smallest usually

found among the catch are 14 or 15 cm. and at Grand Manan 17 or 18 cm. long. The smaller lobsters where present on the fishing ground have escaped through the sides or heads of the trap. Also, as seen in figure 8, the percentage growth of the female on moulting decreases abruptly on the approach of maturity, and since (see figure 4) sexual maturity arrives at different sizes in different areas, the area with the greatest size at maturity will tend to have the largest females and consequently the average size of the lobsters in this area will tend to be larger. Finally, some of our unpublished data show that the proportion of large lobsters to small is greater in deep water than in shallow, consequently averages calculated from deep water catches will tend to be larger than those calculated from catches in shallow water. In producing differences in the average size of lobsters in fishermen's catches from two areas some or all of the above factors may be acting.

The small average sizes in the southern part of the gulf of St. Lawrence as compared with those in southern Nova Scotia may be attributed to a combination of more successful breeding, more intensive fishing in shallower water, to lobsters being first taken at a size several centimetres smaller, and to earlier sexual maturity in the southern gulf than in southern Nova Scotia.

In the Magdalen islands area the smallest average sizes were recorded from Pleasant bay. In this bay are found the highest temperatures in the area (with the exception of the lagoons). Presumably these higher temperatures through a shortening of the defenceless larval period render the area more suitable for larval survival than the neighbouring colder water areas. The largest average size was found at Brion island, where the low temperature is presumably less suitable for successful reproduction, and where fishing is apparently not as intensive as in Pleasant bay.

The large average sizes found in the eastern part of the south coast of Prince Edward Island seem to be largely due to the fact that the fishing grounds in this area are in general offshore in deep water. Conditions near shore are apparently not suitable for a big population of lobsters. Small lobsters are less abundant in deep water, larval survival is presumably less successful in the colder offshore water, and fishing is less intensive than in shallow water areas.

In eastern Cape Breton the small average sizes obtained in the northeastern part were from lobsters caught in the bays and coves. Here also the warm water flowing out of the gulf during the summer would provide conditions very favourable for larval survival. The larger sizes obtained on the southeast coast were caught in considerably deeper water on the open coast where the percentage of small lobsters would be less.

SUMMARY

During the summers of 1930, 1931 and 1932 investigations into the life history of the lobster (*Homarus americanus*), were carried on by the writer on the coast of the Maritime provinces of Canada. Information was obtained by examination of the commercial catches of fishermen in more than one hundred and seventy localities and during special fishing by the writer in various areas. During these investigations many differences were found between local populations of lobsters, these differences and their relation to environmental conditions being summarized below.

HATCHING

A study of data on earliest lobster hatching gathered from the records of lobster hatcheries for fifteen years between 1893 and 1917 shows that hatching in the hatchery jars occurred on the average earliest in western Northumberland strait. The average date of first hatching was from 5 to 10 days later in eastern Northumberland strait hatcheries and at Shippigan in northern New Brunswick, and still later at Inverness and Canso.

The most important factor in determining these differences in the date of first hatching in the hatcheries is the temperature of the bottom water in shallow water areas near the hatchery during the months immediately before and after egg-extrusion, a high water temperature in these areas from June to October being correlated with an early date of first hatching and a lower temperature causing hatching to begin later.

Differences in the dates when natural hatching begins in various areas should be similar to those already described for the hatcheries, but hatching in nature would begin at least a week later than the dates given for hatcheries.

A high summer temperature of the water on the lobster grounds leads to an early completion of natural hatching. Thus, in areas with a very high summer temperature such as Malpeque bay and House Harbour lagoon, hatching is largely completed in early July. In western Northumberland strait with a slightly lower summer temperature the maximum hatching appears to be over by the end of July and hatching is certainly completed before August 20, while in the colder waters of eastern Northumberland strait some hatching may occur even toward the end of September.

EGG-BEARING LOBSTERS

In the whole gulf of St. Lawrence area south of Chaleur bay, in eastern Cape Breton and southwards along the Nova Scotia coast as far as Liscomb, mature female lobsters about 18 to 21 cm. in length may be found. South of St. Margarets and Mahone bays there is an increase in the size of the female at first maturity, this increase continuing until in southern Nova Scotia west of cape Sable and in the bay of Fundy the size of the smallest mature females ranges from 28 to 35 cm.

Apparently the higher summer temperatures in the southern gulf and similar warm water regions are favourable for growth in length of the lobster but even more favourable for ovarian development so that the animal becomes mature at an early age and a small size; while the lower summer temperatures in such areas as Grand Manan are still suitable for digestion and for general body growth but apparently very unfavourable for ovarian development, so that the animal grows to a large size before becoming sexually mature.

Where the size of sexual maturity is large the percentage of the total catch, of lobsters carrying eggs, is small since with intensive fishing few females can reach the size at which sexual maturity begins.

MOULTING

In the regions examined, moulting occurs earliest in Malpeque bay and in the lagoons of the Magdalen islands where a great part of the moulting is over by the end of June. Here also were found the highest summer bottom temperatures. Early summer temperatures on the inshore fishing grounds in Pleasant bay, Magdalen islands, and in Shediac bay, western Northumberland strait, were several degrees lower and the moulting period several weeks later than in Malpeque bay or House Harbour lagoon. The slightly higher summer temperature on the fishing ground in Shediac bay than in Pleasant bay is reflected in the slightly earlier moulting in Shediac bay. The lowest summer temperatures were found at Grand Manan where temperatures about 8°C. lower than in Malpeque bay were found in August, 1932. Correlated with this the first general moulting period at Seal cove, Grand Manan was over two months later than in Malpeque bay.

Such direct correlation between the time of moulting and summer temperature exists in the above areas that the presence of more food in one area than another is probably a very small factor in determining the time of moulting.

In areas with a high summer temperature such as western Northumberland strait and the lagoons of the Magdalen islands, the first moulting period occurs so early that among the fast-growing smaller lobsters of commercial size a second moulting may occur during late summer or early fall. In western Northumberland strait male lobsters as large as 23 to 25 cm. and female lobsters up to 21 or 22 cm. may moult a second time during the year. In areas with a very low summer temperature such as Grand Manan the first moult during the year occurs so late that there is little probability of a second moult even among the smallest commercial sizes.

LENGTH INCREASE ON MOULTING

There is little difference in the growth on moulting of male and female lobsters until sexual maturity approaches when the percentage growth of the female on moulting rapidly decreases below that of the male. Thus in an area such as Pointe du Chêne with early sexual maturity, the decrease in the percentage growth of the female on moulting begins at a much smaller size than at Grand Manan where sexual maturity only occurs at a very large size.

Since the amount of food eaten by the lobster affects its increase in length on moulting, differences in growth on moulting of lobsters in various areas, due to differences in the food supply, may possibly occur.

RELATIVE NUMBERS OF MALE AND FEMALE LOBSTERS AT VARIOUS SIZES

In the region from Chaleur bay to Jeddore, at the smallest commercial sizes (14 to 18.8 cm.), there are more males than females in the catch, possibly due to a greater activity of the males at these sizes. As the size of sexual maturity approaches, the growth rate of the female declines rapidly below that of the male, the female year classes are crowded together and between the sizes 18.8 and 27 cm. more females than males appear in the catches. At sizes beyond 27 cm. the proportion of males in the catch rapidly increases beyond that of the females,

since males of these sizes are considerably younger than females of corresponding size and have run less risk of capture.

In the Seal island area of southern Nova Scotia, at sizes from 16.5 to 24.2 cm., more males than females appear in the catch and at sizes from 24.2 to 32.0 cm. more females than males. In this area it seems probable that the increase in the proportion of females is entirely due to a greater proportion of males being caught at the smaller sizes. At the largest sizes caught the great excess of males seen in the "Chaleur bay to Jeddore" region is not evident in the Seal island area since in this area sexual maturity comes at such a large size (about 32 cm.) that the crowding together of the female year classes only occurs at the largest sizes caught. If the rare individuals of still larger size had been represented in our measurements from the Seal island area, the males at these very large sizes would almost certainly be more numerous than the females.

AVERAGE SIZE

The small average sizes (usually 17.0 to 21.5 cm.) of lobsters in the commercial catches from the southern part of the gulf of St. Lawrence as compared with the larger average sizes (22.2 to 25.1 cm.) of southern Nova Scotia, may be attributed to a combination of more intensive fishing in shallower water, to lobsters being first taken at a size several centimetres smaller, to sexual maturity (with consequent reduction of growth rate, at least in the female lobsters) occurring at a smaller size, and possibly to more favourable temperature conditions for larval survival in the southern gulf area than in southern Nova Scotia and at Grand Manan.

Where the average size varies in the southern gulf area itself, variations in growth due to differences in the size at which sexual maturity first occurs need not be considered as a factor since first sexual maturity seems to occur at approximately the same size throughout the whole area. In some cases, such as in southeast Prince Edward Island, and the northern part of the Magdalen islands, large average sizes of lobsters in the fishermen's catches may be produced by a predominance of deep water fishing grounds where larger lobsters naturally resort and where fishing is less intensive. In other southern gulf fishing areas with warm shallow water, favourable temperatures for larval survival and intensive fishing cause a predominance of small lobsters with consequently a commercial catch with a small average size.

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An Ecological Study of the Sea Mussel (*Mytilus edulis* Linn.)

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(Received for publication November 22, 1935)

ABSTRACT

The distribution of the sea mussel beds of the Passamaquoddy bay area is almost exclusively intertidal. The experiments herein reported show that mussels grow most rapidly when constantly submerged. Their general absence below the low tide level, therefore, is attributed to the particular abundance in this region of the predatory fauna.

The sea mussel (*Mytilus edulis* Linn.) has a general distribution along the Atlantic coast from the sub-arctic regions as far south as cape Hatteras. As a rule the beds of this species extend below the sea from the intertidal belt to a depth of five fathoms (9 m.) or more. In Passamaquoddy bay, however, its habitat is greatly restricted, being almost exclusively intertidal. Records of Verrill and Smith, 1873, show that mussels have been dredged in the bay of Fundy at a depth of fifty fathoms (90 m.). Accounts of Ganong, 1885, indicate that mussels, which grow very abundantly on the intertidal zone around Passamaquoddy bay, "are found at their fullest perfection by dredging in four or five fathoms." Without doubt many dredgings have been made on these grounds since that date, but there are no recent records which indicate that mussels are found below the lowest tidal level. Miss Mossop (1921), who made an extensive survey of the beds of this region, does not report the finding of mussels in any dredgings carried out by her. It is significant, therefore, that in the summer of 1928 the writer was able to gather, from the coralline zone off Big Letite and in L'Etang harbour, several large normally shaped specimens. Mussels do still occur in the deeper waters of Passamaquoddy bay and vicinity, though they are exceedingly rare. The waters of this region are particularly fertile and furnish an abundance of food for a great variety of forms, both vertebrate and invertebrate. It would appear, accordingly, that such an environment would prove very favourable for the luxurious growth and distribution of the sea mussel. That there is an almost general absence of this form below the low tide level indicates that factors other than those directly relating to nutrition play a more significant rôle in regulating the distribution of this species.

It has long been recognized that the natural enemies of a species constitute a positive factor in determining its distribution. When enemy populations are relatively small there is usually maintenance of an equilibrium between the preying types and those which are preyed upon, so that relative stabilization

exists in the numbers of each. If, however, enemies are abundant, there is a reduction in the numbers of the species preyed upon which may continue, at least for a particular area, almost to the point of extermination.

In the Passamaquoddy bay region there are abundant populations of starfishes, sea urchins, whelks, and other invertebrates which feed upon pelecypod molluscs, and upon the sea mussel especially (Huntsman 1918). The flounder (*Pseudopleuronectes*), the eel pout (*Zoarces*), and other such fishes also have to be reckoned with in this connection (Mossop 1921). The question arises, therefore, whether the populations of these enemy forms are sufficiently great to restrict the development of the sea mussel in this region so that it seldom is found below the low water level. If this were so, it would be possible to cultivate mussels below the low tide mark when they were adequately protected against attack from predatory species.

To test this hypothesis, the following experiment was performed at St. Andrews during the summer of 1928. Young mussels, gathered from off *Ascophyllum* and from old weir stakes, were measured in their three dimensions to the nearest tenth of a millimetre, and arranged in four groups (see table I). The average measurements for each group were computed. Thereafter, at intervals of two weeks throughout the summer, the mussels were measured again, and the average increases for each group recorded. Three groups of mussels were placed in locations which differed particularly with respect to the amount of submergence. The control group was placed on the intertidal zone at some distance from the low water mark.

In order to insure maximum protection to the growing mussels, wire cages, 12 in. x 8 in. x 6 in. ($30\frac{1}{2}$ x20x15 cm.) were constructed. These contained two compartments, an outer and an inner. Both were made of galvanized wire screening, with meshes 4 mm. square, and fastened on the bottom to a piece of thick spruce board. The two compartments were separated from one another by at least an inch (2.5 cm.). The inner compartment prevented mussels from escaping or being washed out of the cage, and the outer compartment prevented the near approach of enemy forms. This two-compartment cage was considered a necessary precaution, since small starfish and certain whelks can attack mussels within a cage under some circumstances. The spruce board, with its rough surface, afforded a good substratum for the attachment of the byssus threads of the young mussels. These usually became attached to the bottom of the cages a few hours after being submerged. The cages were anchored in definite positions by heavy weights, and the location of each was indicated by a buoy marker.

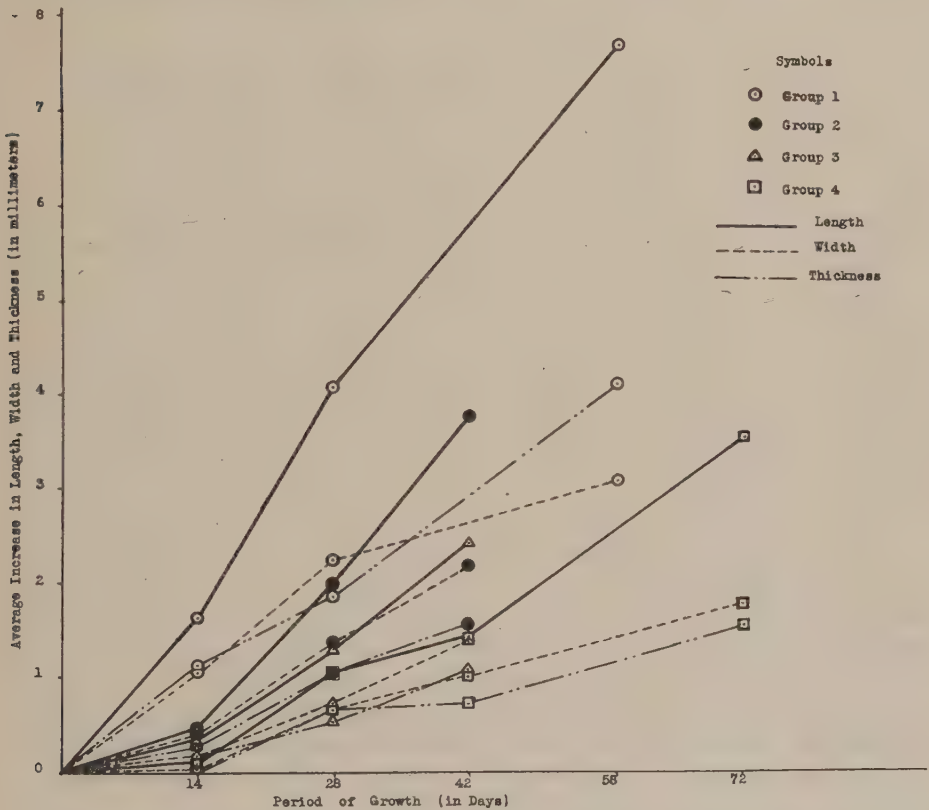
The cages were set out as follows:

Cage I was suspended to the floating breakwater in such a manner that it was regularly exposed to all changes in the movement of the surface water. The bottom of the cage was maintained at a constant depth of fourteen inches ($35\frac{1}{2}$ cm.) below the surface. The mussels were, therefore, under fairly uniform illumination. At intervals it was necessary to remove clusters of floating seaweeds which tended to interfere with the currents passing through the cage, and with the normal penetration of light.

Cage II was anchored to the bottom of the river, south of the laboratory wharf, in a position whereby it was submerged four feet (1.2 m.) at the very lowest tides. The daily submergence accordingly varied on the whole from 4 to 29 feet (1.2 to 8.8 m.).

Cage III was anchored to the river bottom in a location not far from that of cage II. It was, however, placed at a depth that was always 9 feet (2.7 m.) below the lowest tide level.

Cage IV was placed on the intertidal zone where, during the month, its average daily exposure was about four hours.



During the months of July and August the cages were taken up at intervals of fourteen days. The mussels were carefully measured, and then replaced in the original locations. During September the cages were set out for a period of thirty days. Stormy weather prevailed during a part of that month, and cages II and III were lost. The data for these two, therefore, do not go beyond the measurements of the last readings in August. From the measurements, which are given in table I, the average increase for each group was obtained periodically. The increases are indicated in graphic form, for all three dimensions, in figure 1. These indicate quite clearly, for the periods of the experiment, which environments are the most favourable for growth in *Mytilus edulis*.

TABLE I.—Data on the growth of mussels

Date	Group	Number of Individuals	Average measurements in mm.			Increase in mm.		
			Length	Width	Thickness	Length	Width	Thickness
1928								
Aug. 1	I	69	15.13	8.16	5.50			
15		67 (2 died)	16.79	9.20	6.59	1.66	1.04	1.09
29		66 (1 died)	19.22	10.39	7.37	4.09	2.23	1.87
Sept. 28		65 (1 lost)	22.90	11.29	9.62	7.77	3.13	4.12
July 17	II	65	14.53	7.81	5.92			
31		65	15.02	8.21	6.20	0.49	0.40	0.28
Aug. 14		63 (2 died)	16.50	9.16	6.94	1.97	1.35	1.02
28		63	18.26	10.00	7.46	3.73	2.19	1.54
Sept. 28		(Cage lost—no data)						
July 17	III	96	13.27	7.29	5.43			
31		94 (2 died)	13.61	7.45	5.60	0.34	0.15	0.17
Aug. 14		94	14.59	8.01	5.98	1.32	0.72	0.55
28		92 (2*died)	15.73	8.70	6.51	2.46	1.41	1.08
Sept. 28		(Cage lost—no data)						
July 18	IV	66	14.53	7.81	5.88			
Aug. 1		60 (6 died)	14.60	7.85	5.88	0.07	0.04	0.00
15		60	15.55	8.50	6.57	1.02	0.69	0.69
29		60	15.95	8.81	6.61	1.42	1.00	0.73
Sept. 28		60	18.07	9.59	7.46	3.54	1.78	1.58

(*Destroyed by starfish)

The data in table I have been obtained with a reasonable degree of accuracy. In no instance did the mortality exceed nine per cent. A glance at the table and chart readily indicates that the rate of growth of the mussels which are constantly submerged exceeds by far that of the specimens which are exposed for a period between tides. The rate of growth of the specimens in cage I was the greatest, since the location of this cage was such as to insure general uniformity throughout the period of the experiment. The nutrient elements of the plankton are, in general, more abundant near the surface. These results, as tabulated, concur with observations made by Miss Mossop (1921).

The normal environment for mussel beds appears to be that of a submerged region such as the shallow bottom of a bay or river. The results obtained for cages II and III, therefore, have great significance in the interpretation of the data, and particularly since it has been demonstrated that mussels will grow under submerged conditions in Passamaquoddy bay. In the places where these cages were set out, there were variations in the amount of penetration of light, as well as in the amount of food available at different periods of the day. The phytoplankton upon which the mussel feeds tends to rise near to the surface during the daytime. The growth of mussels in cage II, which was nearer to the shore line, was more rapid than it was for those in cage III, which was the deeper

and the more remote. This observation is in accord with the statement of Miss Mossop (1921) that mussels near to the surface showed more rapid growth (in length) than did those in the deeper regions. In both cases, however, the rate of growth greatly exceeded that of the mussels in cage IV, which was placed on the intertidal zone. The increase in length in the mussels of the latter case, for a period of seventy-two days, was not equal to the increase in length in the mussels in cage II for only forty-two days. Growth in the mussels of the intertidal zone was greatly suppressed. This accords with the finding of Coulthard (1929), who says, "Exposure (*i.e.*, curtailment of food and oxygen supply, and rise of temperature) even for a short period every day has an inhibitory effect on growth."

Cages anchored below low tide level were constantly surrounded by starfishes, sea urchins, and whelks (*Buccinum undatum*, etc.). It is probable that shortly after mussel spat has found attachment at points below the low tide level (and it appears to settle quite generally both above and below low water level) young mussels are attacked and devoured in large numbers by their natural enemies so that they have little opportunity for becoming established in beds. Only in those places where they are not so molested, as on the lower border of the intertidal belt, do they actually gain a foothold.

Growth took place more rapidly in those mussels which were protected by cages anchored to the bottom of the river (which would seem to be the natural location for submerged mussel beds) than in the case of mussels growing on the intertidal zone. This evidence, therefore, supports quite definitely the view (Huntsman 1918) that the depredations of the numerous natural enemies of the mussel are largely responsible for the general absence of its beds below the low tide mark in the vicinity of St. Andrews and Passamaquoddy bay.

It is interesting to note that the valves of mussels subjected to exposure and to much light are modified in form. (See graph for cage I.) This was seen particularly in the case of those mussels in cage I, which was submerged at a constant depth of fourteen inches ($35\frac{1}{2}$ cm.). There was the tendency for the growth in the thickness between the valves to exceed that in the width (depth) of the valves. This was observed, also, in the case of the specimens growing on the intertidal zone. Mussels more deeply submerged were in more subdued light and did not show such disproportion in their growth. These appeared to develop the "normal" shape of valve, thus contrasting with the "St. Andrews" type as is found on the littoral zones. These observations concur with statement of Mr. Coulthard, that the shells of mussels grown in the sunlight have greater thickness but less depth than those grown in subdued light. Professor Huntsman (1921) believes that strong light rays injure the tissues of the mussel, and that such injury is most effective upon the more or less exposed growing edge of the mantle. It would appear that this inhibition to the normal growth of the free edge of the mantle is compensated for in part by the "rolling in" of the edges of the valves, hence a disproportionate increase in the thickness between the valves results.

SUMMARY

1. It has been shown by experiments that sea mussels, protected against invasion from predatory organisms, have more rapid rates of growth when constantly submerged than when exposed between tides, even for brief periods daily.

2. From the data it appears evident that the general absence of mussel beds below the low tide level of Passamaquoddy bay is the result of the almost total destruction of young mussels by their numerous natural enemies.

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